

14:40:41

OCA PAD INITIATION - PROJECT HEADER INFORMATION

09/10/10

Project #: E-19-801
Center #: T5153-OA0Cost share #: E-19-344
Center shr #: J5153-OA0Active
Rev #: 0
OCA file #:
Work type : PUB SER
Document : AGR
Contract entity: GTRCContract #: AGR DTD 870601
Prime #:

Mod #:

Subprojects ? : N
Main project #:Project unit:
Project director(s):
POEHLEIN G WCHE
CHE

Unit code: 02.010.114

Sponsor/division names: DOW CHEMICAL COMPANY
Sponsor/division codes: 203/
/ 014

Award period: 870601 to 880531 (performance) 880531 (reports)

Sponsor amount	New this change	Total to date
Contract value	33,917	33,917
Funded	33,917	33,917
Cost sharing amount		2,960

Does subcontracting plan apply ? : N

Title: EMULSION POLYMERIZATION WITH VINYL ACID MONOMERS

PROJECT ADMINISTRATION DATA

OCA contact: Earnestine P. Smith

894-4820

Sponsor technical contact

Sponsor issuing office

DR. BRUCE K. DIETRICH
(517)636-0773
THE DOW CHEMICAL COMPANY
DESIGNED LATEX & RESINS - MAS&
1604 BLDG. MIDLAND, MI 48640THE DOW CHEMICAL COM
(517)636-0773
1776 BUILDING
MIDLAND, MI 48674Security class (U,C,S,TS): U
Defense priority rating: NA
Equipment title vests with Sponsor
NOT APPLICABLE TO THIS PROJECTONR resident rep. is ACO (Y/N): N
NA supplemental sheet
GIT

Administrative comments -

THE AWARD INCLUDES AN \$18,000 FELLOWSHIP. THE FELLOWSHIP IS BUDGETED IN
MATERIALS & SUPPLIES PER INSTRUCTIONS FROM DAVID WELCH.
CONSULTANTS AND SUBCONTRACTS REQUIRE PRIOR SPONSOR APPROVAL.

SPONSORED PROJECT TERMINATION/CLOSEOUT SHEETDate 8/5/88Project No. E-19-801 T-5153-OAO School/~~Lab~~ ChEIncludes Subproject No.(s) N/AProject Director(s) G. W. Poehlein GTRC/GITSponsor Dow Chemical CompanyTitle Emulsion Polymerization with Vinyl Acid MonomersEffective Completion Date: 5/31/88 (Performance) 5/31/88 (Reports)

Grant/Contract Closeout Actions Remaining:

☐ None☒ Final Invoice or Copy of Last Invoice Serving as Final☐ Release and Assignment☒ Final Report of Inventions and/or Subcontract:
Patent and Subcontract Questionnaire
sent to Project Director ☒☐ Govt. Property Inventory & Related Certificate☐ Classified Material Certificate☐ Other _____Continues Project No. _____ Continued by Project No. E-19-641

COPIES TO:

Project Director
Research Administrative Network
Research Property Management
Accounting
Procurement/~~GTRC~~ ~~Supply~~ ~~Services~~
~~Research~~ ~~Administrative~~ ~~Network~~
Reports=Coordinator (OCA)
~~Program~~ ~~Administrative~~ ~~Division~~
Contract Support Division (2)

~~Research~~ ~~Administrative~~ ~~Network~~ ~~Management~~ ~~XXX~~ ~~ERS~~
Library
GTRC
Project File
Other _____



Georgia Institute of Technology

A UNIT OF THE UNIVERSITY SYSTEM OF GEORGIA

ATLANTA, GEORGIA 30332-0370

OFFICE OF VICE PRESIDENT
FOR RESEARCH

October 20, 1987

To: OCA Reports Coordinator/CRB

From: Gary W. Poehlein, Associate Vice President
for Graduate Studies and Research

Subject: Report/Project No. E-19-801

The first deliverable on Project E-19-801 was a "Work Plan." The attached Ph.D. thesis proposal entitled "Batch Emulsion Copolymerization with Carboxylic Acids" was submitted to Dr. Bruce Dietrich during his last visit to Georgia Tech. Dr. Dietrich will serve on Mr. Shoaf's thesis committee. This thesis proposal is, in effect, the "Work Plan" under Project E-19-801.

GWP:sd

Enclosures

BATCH EMULSION COPOLYMERIZATION WITH CARBOXYLIC ACIDS

A PhD Thesis Proposal

by Glenn Shoaf

Georgia Tech Committee Members:

Dr. Gary W. Poehlein (Chairman)

Dr. F. Joseph Schork

Dr. Eric J. Clayfield

Dr. Malcolm B. Polk (Textile Engineering)

Dr. Laren M. Tolbert (Chemistry)

School of Chemical Engineering
Georgia Institute of Technology

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
I. INTRODUCTION	1
II. THEORY	3
a. Homopolymerization	3
b. Polymerization of Carboxylic Acids	4
c. Emulsion Polymerization Kinetics	11
d. Homogeneous Nucleation	14
e. Copolymerization	20
f. Copolymer Composition	25
g. Emulsion Copolymerization Kinetics	28
h. Homogeneous Particle Nucleation with Emulsion Copolymerization	30
i. Emulsion Copolymerization with Carboxylic Acid	32
III. EXPERIMENTAL	44
a. Homopolymerization Studies of AA and MAA	44
b. Copolymerization Studies of Hydrophobic Monomers (i.e. Styrene) with Carboxylic Acid Monomers	49
c. Particle Nucleation	53
IV. PROPOSED WORK	58
a. Proposed Kinetic Models	63
b. Proposed Experimental Work	68
V. NOMENCLATURE	74
VI. REFERENCES	77

I. INTRODUCTION

Carboxylated copolymer latexes are becoming increasingly important in industry as the demand for specialty chemicals increases. These latexes are often the key components in specialty coatings and thickeners. Carboxyl monomers also aid in particle stabilization.

The addition of a carboxyl monomer to a copolymer latex system magnifies the complexity of emulsion reaction mechanisms. Polymerization in both the particle and aqueous phases must be considered. Reaction rates become dependent on an additional parameter, pH. The ionized acid monomer represents an additional reacting species which must be considered. It exhibits a different reactivity from that of the un-ionized acid. Adequate quantitative models describing the kinetics and particle nucleation mechanisms in these systems are lacking due to their increased complexity compared to more conventional emulsion systems.

The reaction behavior of carboxylated monomers differs from conventional systems not only in copolymerization in emulsion, but also in homo- and copolymerization in solution due primarily to the effect of the additional parameter, pH, on the kinetics. Therefore, in order to fully understand and characterize these systems, an understanding of both homo- and copolymerization reactions involving carboxylic acid monomers is required.

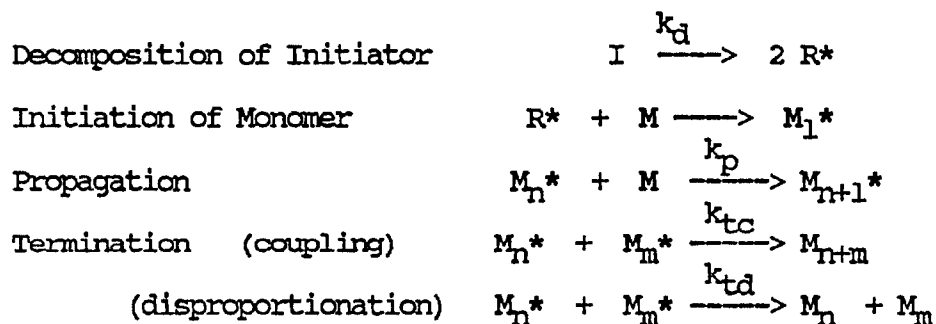
This report presents basic theories of homopolymerization, emulsion polymerization, copolymerization, emulsion copolymerization

and application of these topics to systems involving carboxylic monomers. Included are reviews of both theoretical and experimental work. Suggestions for additional work in this area are also included. Ideas relating to the development of a quantitative kinetic model are proposed.

II. THEORY

Homopolymerization

Free radical chain homopolymerization consists of three basic steps - initiation, propagation, and termination. The following reactions characterize these steps.



Termination may occur by coupling or disproportionation, though termination by coupling is more frequent with many common monomer systems. The rate of reaction for homogeneous, constant volume systems can be described by the following expression [1],

$$R_p = -d[M]/dt = k_p [M] ((f k_d [I])/k_t)^{1/2} \quad (1)$$

with $k_t = k_{tc} + k_{td}$ and f is the initiator efficiency factor.

For a variable volume, homogeneous system, eq. (1a) must be used.

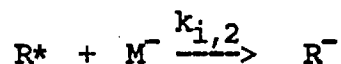
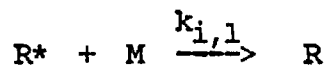
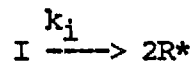
$$R_p = -1/V d\{V[M]\}/dt \quad (1a)$$

The rate is proportional to the first power of the monomer concentration and the one-half power of the initiator concentration. This rate expression is applicable to most homogeneous bulk or solution free radical polymerization reactions although the rate coefficients can vary with conversion due to the changing nature of the reaction environment, i.e. the gel effect.

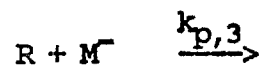
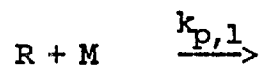
Polymerization of Carboxylic Acids

Carboxylic acids such as acrylic acid (AA) and methacrylic acid (MAA) are completely soluble in water. Therefore, Galperina et. al [2,3] used eq. (1) to describe the kinetics of solution polymerization of these acids. Katchalsky and Blauer [4] reported that the polymerization rate of AA and MAA depends additionally on pH because it involves reaction of both undissociated and dissociated monomer and radical species. The reaction scheme must be expanded for this case to include the undissociated acid (M) and anion (M^-) species. The resulting set of reactions follows the same form as a set of copolymerization reactions.

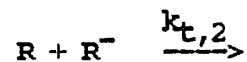
Initiation



Propagation



Termination



Katchalsky and Blauer developed a general rate expression for the homopolymerization of carboxylic acids. Their expressions for the undissociated and dissociated monomer species (M , M^-) and the undissociated and dissociated radical species (R , R^-) are given by equations (2a) and (2b).

$$M = (1 - \alpha) M_t \quad ; \quad M^- = \alpha M_t \quad (2a)$$

$$R = (1 - \beta) R_o \quad ; \quad R^- = \beta R_o \quad (2b)$$

where

M_t is the total monomer concentration

R_o is the total radical concentration

α is the fraction of dissociated acid monomer

β is the fraction of dissociated radicals

The following general rate equation was derived based on a steady-state radical concentration.

$$\frac{-dM_t}{dt} = \frac{(k_d[I])^{1/2} M_t [k_{p,1}(1-\alpha)(1-\theta) + k_{p,2}\theta(1-\alpha) + k_{p,3}\alpha(1-\theta) + k_{p,4}\alpha\theta]}{[k_{t,1}(1-\theta)^2 + k_{t,2}\theta(1-\theta) + k_{t,3}\theta^2]^{1/2}} \quad (2c)$$

Katchalsky and Blauer then simplified this expression by assuming that (i) termination between two ionized radicals is unlikely because of the repulsive forces (ii) the polymer radical is a weak acid such that its degree of ionization is low ($\theta \approx 0$), and (iii) $k_{p,3} = k_{p,4} = 0$ ($k_{p,3}$ and $k_{p,4}$ are the rate constants for reaction of ionized monomer with un-ionized and ionized radicals respectively) since at a high degree of ionization for the monomer ($\text{pH} > 5.5$), the polymerization rate is nearly zero (when H_2O_2 is the initiator). The resulting rate expression is proportional to the fraction of undissociated acid ($1-\alpha$).

$$-dM_t/dt = k_{p,1} [k_d/k_{t,1}]^{1/2} [I]^{1/2} [M] (1-\alpha) \quad (2d)$$

A term for the initiator efficiency, f , is not included. This term should be used for completeness. The corresponding expression for the instantaneous degree of polymerization (D.P.) at time t is given by eq. (3).

$$D.P./(1 - \alpha) = 1.5 k_{p,1} [k_d k_{t,1}]^{-1/2} ([M]_0 + [M_t]) [I]^{-1/2} \quad (3)$$

Pinner [5] reported that the absence of polymerization at a pH of 5.5, which led to assumption (iii), was probably due to inactivation of H_2O_2 , the initiator used by Katchalsky and Blauer in their studies. Pinner shows that reaction occurs at pH as high as 13 if persulfate is used despite the ionization of the monomer. Blauer [6], in a later article, stated that his original statement that ionized monomer is unable to propagate polymerization was in error. He performed runs using AIBN as initiator and obtained polymerization at a pH as high as 12. He also showed that above a pH of 7, the rate constant can be expressed by eq. (3a), assuming that the growing radical behaves electrochemically like a polymeric acid.

$$\frac{-dM_t}{dt} \propto \frac{k_{p,3} (1 - \beta) + k_{p,4} (\beta)}{[k_{t,1} (1 - \beta)^2 + k_{t,2} \beta (1 - \beta) + k_{t,3} \beta^2]^{1/2}} \quad (3a)$$

α is approximately equal to 1 at a pH of 7, but β does not approach 1 until higher values of pH if the polymeric radical is indeed a weaker acid than the monomer. When β does approach 1, the reaction rate then becomes proportional to $k_{p,4}/(k_{t,3})^{1/2}$.

Pinner [5] observed that the polymerization rate of methacrylic acid initiated with potassium persulfate does decrease with increasing pH. He performed copolymerization experiments with amine monomers and acrylonitrile using both the undissociated and dissociated forms of

MAA and found that the anion exhibited a lower rate of reactivity than the undissociated acid. He attributed the decrease in polymerization rate with increased pH to copolymerization of the undissociated acid with its less reactive anion. He then applied the rate equation for copolymerization (4) (assuming chemically controlled termination) to the case of the undissociated MAA (M_a) copolymerizing with its anion (M_b), eq. (4).

$$\frac{-d(M_a + M_b)}{dt} = \frac{(r_a M_a^2 + 2M_a M_b + r_b M_b^2) R_i^{1/2}}{(r_a^2 \delta_a^2 M_a^2 + 2\phi r_a r_b \delta_a \delta_b M_a M_b + r_b^2 \delta_b^2 M_b^2)^{1/2}} \quad (4)$$

where,

$$r_a = k_{aa}/k_{ab}, \quad r_b = k_{bb}/k_{ba}, \quad \delta_a^2 = k_{ta}/k_{aa}^2, \quad \delta_b^2 = k_{tb}/k_{bb}^2$$

and

$$\phi = k_{ta,b}/(k_{ta}k_{tb})^{1/2} = \text{cross termination coefficient}$$

Pinner noted that eq. (2c) developed by Katchalsky and Blauer reduces to eq. (4) if $k_{p,2}$ is set equal to $k_{p,3}$ and if β is set equal to α . He expressed the overall rate constant (K_α defined by eq. (5)) as a function of α by replacing M_a with the undissociated acid concentration $A(1 - \alpha)$ and M_b with the anion concentration $A\alpha$, where A is the total monomer concentration.

$$K_\alpha = \frac{[r_a (1 - \alpha)^2 + 2\alpha(1 - \alpha) + r_b \alpha^2]}{[r_a^2 K_a^{-2} (1 - \alpha) + 2\phi r_a r_b K_a^{-1} K_b^{-1} \alpha(1 - \alpha) + r_b^2 K_b^{-2} \alpha^2]^{1/2}} \quad (5)$$

where $K_a = R_i^{1/2} / \delta_a$ = overall homopolymerization rate constant for the acid

$K_b = R_i^{1/2} / \delta_b$ = overall homopolymerization rate constant for the anion

Finally, using Q and e values (obtained from separate copolymerizations with other monomers such as acrylonitrile and various amines) to calculate r_a ($=0.66$) and r_b ($=0.08$) and replacing K_a and K_b with the observed values, 1.53 and 0.12, respectively, Pinner obtained the following expression for the overall rate constant for MAA as a function of pH:

$$K = \frac{[0.66 (1 - \alpha)^2 + 2 \alpha(1 - \alpha) + 0.08 \alpha^2]}{[0.185 (1 - \alpha)^2 + 0.575 \phi \alpha(1 - \alpha) + 0.445 \alpha^2]^{1/2}} \quad (6)$$

was determined from measured values of pH with the expression,

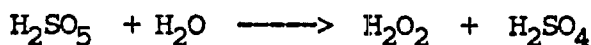
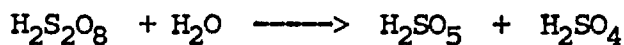
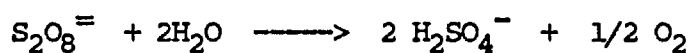
$$\text{pH} = \text{p}K_a + \log (\alpha / 1 - \alpha)$$

where $\text{p}K_a=4.36$ for MAA. Values of ϕ are listed in [7]. The rate expression for homopolymerization of acids can then be expressed as a function of the overall monomer concentration (M_t) and α (via pH) which are both easily measurable.

A decreasing decomposition rate of the initiator with increasing pH may also attribute to a decrease in polymerization rate. Katchalsky and Blauer [4] observed that the polymerization rate of MAA approached zero at a pH of about 6. This was later attributed to deactivation of

the initiator, H_2O_2 [5].

Pinner [5] stated that the decomposition of persulfate did not seem to be adversely affected as the pH increased. In fact it appeared to increase somewhat with pH. Kolthoff and Miller [8] show that the following persulfate decomposition reactions (or side reactions) are suppressed as the $[\text{H}^+]$ decreases (pH increases).



The effect of $[\text{H}^+]$ ion on the rates of the above reactions was studied and a rate equation was proposed:

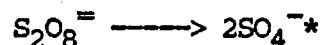
$$-d(\text{S}_2\text{O}_8^{=})/dt = k_1[\text{S}_2\text{O}_8^{=}] + k_2[\text{H}^+][\text{S}_2\text{O}_8^{=}] \quad (7)$$

The overall rate constant is given by,

$$k_o = k_1 + k_2[\text{H}^+] = f(\text{pH}) \quad (8)$$

Experimental values of k_o versus $[\text{H}^+]$ verified this linear relationship.

The relationship of pH to the basic decomposition reaction of persulfate to form free radicals,



was not addressed by these workers. As noted earlier Pinner [5] suggested that decomposition of persulfate to form free radicals is not greatly affected by pH. Kolthoff and Miller [8] do, however, note that the sulfate ion radical can react in another way:



Van den Hul and Vanderhoff [9] reported that the relative number of hydroxyl end-groups formed does increase in the pH range 2 to 10, and the number of sulfate end-groups decreases. Both groups are found in the polymer when styrene is polymerized in an emulsion [9]. Since both species are capable of initiating polymerization, the overall polymerization rate may not necessarily change despite the change in identity of the radical species.

Emulsion Polymerization Kinetics

The first important scheme for emulsion polymerization was depicted by Harkins [10]. The reaction was divided into three intervals. During Interval I particles are nucleated when free radicals generated in the aqueous phase are captured by monomer swollen emulsifier micelles. As polymerization takes place monomer diffuses from the monomer droplets to the growing particles. The particles continue to grow until all of the emulsifier is adsorbed onto the surface of the particles, at which point Interval I ends. During Interval II, monomer continues to diffuse to the growing polymer particles until the monomer droplets disappear. Finally, during

Interval III, further polymerization occurs within the particles until the reaction reaches the final conversion.

The first kinetic theory for emulsion polymerization was proposed by Smith and Ewart [11] and modified by Stockmayer [12]. The Smith-Ewart theory was based on Harkins' mechanism for particle nucleation and growth. Smith and Ewart developed a recursion equation which relates N_{n-1} , N_n , N_{n+1} , and N_{n+2} to the absorption rate for radical entry into particles, the desorption rate for radical transfer out of particles, and the termination rate for radicals in the particles:

$$Nn(\rho_A/N + nk_d + n(n-1)k_t/V_p) = N_{n-1}(\rho_A/N) + (n+1)k_d N_{n+1} + (n+2)(n+1)(k_t/V_p)N_{n+2} + \dots \quad (9)$$

$$\text{where } N = \sum_{n=0}^{\infty} N_n \quad (10)$$

$$(10)$$

and N_n is the number of polymer particles per unit volume of aqueous phase which contains n free radicals, ρ_a is the overall rate of radical absorption by the particles, V_p the particle volume, k_{da} is a rate coefficient for radical desorption from the particles, and k_t is the radical termination constant in the particles. Smith and Ewart then obtained solutions to this equation for three limiting cases:

$$\text{Case 1} \quad n \ll 1.0 ; N_0 \gg N_1 \gg N_2$$

Case 2 $n = 0.5$; $N_0 = N_1$, $N_2 = N_3 = N_n = 0$

Case 3 $n \gg 1.0$

where n is the average number of free radicals per particle. Smith and Ewart, using the Case 2 model, developed the following equations to describe the polymerization rate and average radical life:

$$R_p = k_p[M]_p[R^*] = k_p[M]_p(0.5 N/N_A) \quad (\text{moles/L}_w \cdot \text{sec}) \quad (11)$$

$$\tau_p = N/(2 \rho_A) \quad (\text{sec}) \quad (12)$$

where R_p is the polymerization rate per volume of aqueous phase, k_p is the propagation constant, $[M]_p$ is the monomer concentration in the particles, $[R^*]$ is the concentration of free radicals, and τ_p is the "average" life of a free radical in the polymer particles. Smith and Ewart also developed an expression for the particle number:

$$N = k_N (\rho_i / \mathcal{U})^{0.4} (a_s N_A [S_e])^{0.6} \quad (\text{particles/L-water}) \quad (13)$$

where \mathcal{U} is the rate of volume increase of the particles during Interval I, ρ_i is the rate of generation of free radicals in the water phase, a_s is the surface area occupied by one emulsifier molecule, $[S_e]$ is the concentration of emulsifier, and k_N is a constant between 0.37

and 0.53.

Stockmayer [12] and O'toole [13] presented general solutions to the Smith-Ewart equations (9,10). Ugelstad [13] expanded the generality of these solutions by considering radical desorption from the polymer particles, reabsorption, and termination in the aqueous phase. These works, however, apply only to monodisperse latex.

Homogeneous Nucleation

The Smith-Ewart theory was found to be inadequate for monomers which have a significant degree of water-solubility. Fitch [15] and Priest [16] developed another theory which involved homogeneous nucleation of particles. This theory predicts the number of particles formed when the monomer is partially water-soluble and/or when no surfactant micelles are present. The basic points comprising this theory are listed below.

1. Polymerization in the aqueous phase is the initial process.
2. An oligomer grows to a critical length beyond which it is no longer soluble in water, and it precipitates to form a particle.
3. Surfactant serves not as a nucleating agent, but as a stabilizer of the primary particles.
4. Oligomer chains may combine with polymer particles before nucleation and/or before adequate stabilization.
5. Some particles may coagulate depending on the quantity and effectiveness of the emulsifier.
6. The ultimate particle size depends on the stabilizing effects of

emulsifier plus sulfate groups contributed by initiator.

7. Most of the polymerization occurs within the swollen polymer particles (99.9%).

Assumption 7 is probably not true for systems involving monomers such as carboxylic acids which have a high degree of water-solubility.

Fitch and Tsai [17] developed a quantitative treatment of the homogeneous nucleation theory. They assumed that there are three competitive processes whose rates are radical generation (R_i), radical capture by existing particles (R_c), and particle flocculation (R_f). The rate of particle formation then becomes,

$$dN/dt = R_i - R_c - R_f \quad (14)$$

No particles are present in the initial stages of reaction so that $dN/dt = R_i$. Later, when particles are present, some oligomeric radicals will be captured by these particles. When more particles form, flocculation will occur if they are not sufficiently stabilized.

Fitch and Tsai [17] derived eq. (15) for the rate of capture, R_c .

$$R_c = \pi R_i L N r_p^2 \quad (15)$$

where,

R_i = rate of initiation

N = number of particles

r_p = radius of particle

L = distance traveled during the time needed for polymerization to the critical chain length.

$$L = (2Dt)^{1/2} = [(2D DP_{\max})/(k_p[M])]^{1/2} \quad (16)$$

where,

D = monomer diffusion coefficient

t = time

DP_{\max} = maximum degree of polymerization before precipitation.

They assumed that every collision of a radical with a particle leads to capture of that radical. Using geometrical relationships and an expression for particle growth, R_c is rewritten as a function of monomer concentration and time and substituted into eq. (13). Assuming that flocculation is negligible (i.e. particles formed are well stabilized) the rate of particle formation becomes:

$$dN/dt = R_i \{1 - (N/\pi)^{1/3} [3/4 (k_p/k_t)^{1/2} \ln[\cosh(R_i k_t)^{1/2} t]^{2/3} L]\} \quad (17)$$

Integration yields the final number of particles,

$$N = \int_0^{t_{\max}} (dN/dt) dt \quad (18)$$

where t_{\max} is the time where N reaches a maximum.

Eq. (17) does not account for flocculation and particle capture. Fitch and Tsai discuss limited flocculation theory. Flocculation, in general, will occur if there is a lack of sufficient repulsion between the particles. They note that flocculation in ionically stabilized systems will occur until a critical surface potential ψ_c is developed.

ψ_c is related to the surface area per ionic group (polymer chain ends plus surfactant), A_g . A_g depends on the chain length and the endgroups (i.e. initiator used). As flocculation continues clusters of particles form whose total potential rises (due to decreased total surface area and subsequent increase in charge density on the surface) until 'stabilization' occurs.

Homogeneous nucleation theory was expanded by Hansen and Ugelstad [18]. They proposed the following equations for radical growth and capture for the case where no seed particles are present:

$$dR_1/dt = \rho_i - k_{pi}M_wR_1 - k_{twi}R_1R_{tot} \quad (19)$$

$$dR_1/dt = k_{pw}M_wR_1 - k_{pw}M_wR_1 - k_{cl}NR_1 - k_{twi}R_1R_1 - k_{tw}R_1R_{tot} \quad (20)$$

$$dR_j/dt = k_{pw}M_wR_{j-1} - k_{pw}M_wR_j - k_{cj}NR_j - k_{twi}R_jR_1 - k_{tw}R_jR_{tot} \quad (21)$$

When j reaches j_{cr} , the critical chain length for particle nucleation occurs, and the polymer chain precipitates. Primary particle formation is then described by eq. (22).

$$dN_1/dt = k_{pw}M_wR_{j_{cr}-1} \quad (22)$$

Considering the rate of coagulation of primary particles with themselves, ρ_c , the total number of particles is described by eq. (23).

$$dN/dt = dN_1/dt - \rho_c \quad (23)$$

The total concentration of oligomer radicals in the aqueous phase is defined by

$$[R_{\text{tot}}] = \sum_{j=1}^{j_{\text{cr}}-1} [R_j] \quad (24)$$

Ugelstad et al. assumed a steady-state for all radicals R_j up to $R_{j_{\text{cr}}-1}$ neglected termination with initiator radicals, and assumed that an average rate constant for radical capture can be used, \bar{k}_C ,

$$k_C = \sum_{j=1}^{j_{\text{cr}}-1} k_{Cj} R_j / R_{\text{tot}} \quad (25)$$

The resulting expression for the rate of particle formation follows:

$$\frac{dN_1}{dt} = \frac{\rho_i}{[1 + (\bar{k}_C N) / (k_p M_w) + (k_{tw} R_{\text{tot}}) / (k_p M_w)]^{j_{\text{cr}}-1}} \quad (26)$$

At low values of $[M]_w$, R_{tot} may be defined by

$$R_{\text{tot}} = \{[(\bar{k}_C N)^2 + 4 \rho_i k_{tw}]^{1/2} - \bar{k}_C N\} / 2k_{tw} \quad (27)$$

In order to obtain an analytical solution, they also assumed a steady-state concentration of radicals in the aqueous phase and considered termination only in this phase such that:

$$R_{\text{tot}} = (\rho_i / k_{tw})^{1/2} \quad (28)$$

Eq. (26) could then be solved directly to give an expression for N_1 .

$$N_1(t) = (1/k_1) \{ [k_1 \rho_i j_{cr} t + (k_2 + 1) j_{cr}]^{1/2} j_{cr} - k_2 - 1 \} \quad (29)$$

where $k_1 = \bar{k}_O/k_p M_w$ and $k_2 = (k_{tw} \rho_i)^{1/2}/k_p M_w$

Approximations made to arrive at this solution included: (i) no coagulation, (ii) irreversible absorption of radicals, (iii) termination only in the water phase, and (iv) steady-state concentration of radicals in the water phase. They compared the analytical solution to the numerical solution obtained when steady-state was not assumed. The analytical solution proved to be rather inadequate.

Hansen and Ugelstad [18] stated that for a seeded system radicals will be captured by particles according to the number and size of the particles. Assuming a mean value for the capture constant, k_{CS} , the total adsorption of radicals in the seed particles is,

$$\rho_{CS} = \bar{k}_{CS} N_S R_{tot} \quad (30)$$

Eq. (30) is approximately equal to the total capture rate for a large number of seed particles. Using eq. (31) to express the steady-state value of R_{tot} :

$$R_{tot} = \{ [(\bar{k}_{CS} N_S)^2 + 4 \rho_i k_{tw}]^{1/2} - \bar{k}_{CS} N_S \} / 2 k_{tw} \quad (31)$$

an equation for dN_1/dt was derived:

$$\frac{dN_1}{dt} = \frac{\rho_i}{\left\{1 + \frac{(\bar{k}_c N)}{k_p M_w} + \frac{\bar{k}_{cs} N_s}{2k_p M_w} + \left[\frac{(\bar{k}_{cs} N_s)^2 + 4\rho_i k_{tw}}{2k_p M_w}\right]^{1/2}\right\}^{j_{cr}-1}} \quad (32)$$

which upon integration gives

$$N_1 = (1/k_1) \{ [k_1 \rho_i t + (0.5k_s N_s + (0.25k_s^2 N_s^2 + k_2^2)^{1/2} + 1)^{j_{cr}}]^{1/j_{cr}} - 0.5 k_s N_s - (0.25k_s^2 N_s^2 + k_2^2)^{1/2} - 1 \} \quad (33)$$

where k_1 and k_2 are the same as in eq. (29) and $k_s = \bar{k}_{cs}/k_p M_w$.

Though coagulation is not included in the above models, Hansen and Ugelstad discussed particle coagulation theory in some detail in the same article [18].

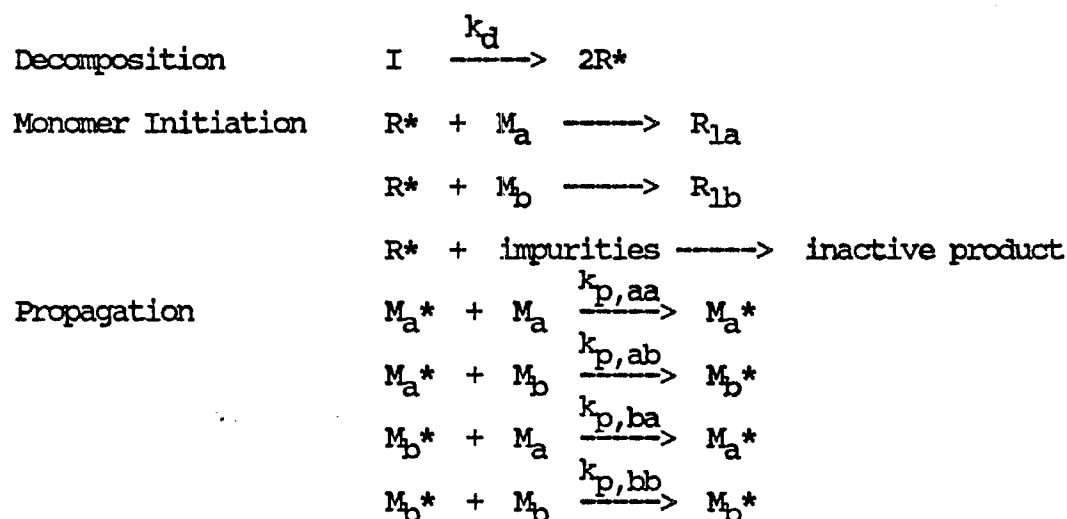
An exhaustive review of particle nucleation mechanisms and models with references has been prepared by Song [19]. This review includes basic descriptions of additional work done by Arai (emulsifier-free systems), Kao (radical capture efficiencies), Feeney (two step coagulative nucleation model), and others.

Copolymerization

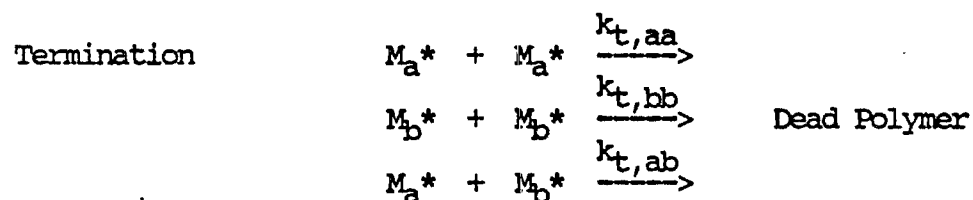
An extensive amount of work has been reported for copolymerization of monomers using free radical initiators. A brief review of the basic

kinetic and composition equation for copolymers formed in bulk or solution is included in this section.

The basic initiation and propagation reactions for copolymerization of two monomers, M_a and M_b follow:



Termination may be either chemical controlled or diffusion controlled. Melville [20] and Walling [21] developed kinetic expressions for chemical controlled termination.



Several basic assumptions apply. (1) Steady-state concentration is assumed for each type of radical. Hence, $k_{ba}[M_b^*][M_a] = k_{ab}[M_a^*][M_b]$. (2) Steady state is assumed for the total concentration of radicals. (3) Rate constants for the reaction of a growing chain depend only on the monomer on the end and not on the length of the

chain or composition of the chain. The propagation rate constants are combined as follows into reactivity ratios:

$$r_a = k_{aa}/k_{ab} , \quad r_b = k_{bb}/k_{ba}$$

A rate expression can then be derived.

$$R_p = \frac{-d([M_a] + [M_b])}{dt} = \frac{(r_a[M_a]^2 + 2[M_a][M_b] + r_b[M_b]^2)R_i^{1/2}}{\{r_a^2 \delta_a^2 [M_a]^2 + 2\phi r_a r_b \delta_a \delta_b [M_a][M_b] + r_b^2 \delta_b^2 [M_b]^2\}^{1/2}} \quad (34)$$

$$\text{where } \delta_a = (k_{taa}/k_{aa}^2)^{1/2} , \quad \delta_b = (k_{tbb}/k_{bb}^2)^{1/2} ,$$

$$\text{and } \phi = k_{tab}/[2(k_{taa} k_{tbb})^{1/2}]$$

Note that δ = reciprocal of $k_p/k_t^{1/2}$ for homopolymerization.

It later became well-established that termination in radical polymerization can be diffusion controlled [22,23,24]. Therefore, ϕ is not constant with composition and use of a single ϕ value in the rate expression may produce dubious results. Atherton and North [25] presented the termination reactions and corresponding kinetic expression associated with diffusion controlled termination.

Termination



k_{tab} is a function of the copolymer composition and for the ideal case, eq. (35) may be used.

$$k_{tab} = F_a k_{taa} + F_b k_{tbb} \quad (35)$$

See eq. (40) for the expression for F_i .

Again the steady-state assumption for radicals is made,

$$R_i = 2 k_{tab} ([M_a^*] + [M_b^*])^2 = 2k_{tab} ([M_a^*] + [M_b^*])^2 \quad (36)$$

Using the definition of reactivity ratios, North develops a kinetic expression, eq. (37).

$$R_p = \frac{(r_a [M_a]^2 + 2 [M_a] [M_b] + r_b [M_b]^2) R_i^{1/2}}{k_{tab}^{1/2} \{ (r_a [M_a] / k_{aa}) + (r_b [M_b] / k_{bb}) \}} \quad (37)$$

Extensions of diffusion controlled copolymerization reaction theory are presented by Hamielec and co-workers [51,52,53]. They stated that at low conversions segmental diffusion controls the termination rate, and as the reaction proceeds, the termination rate becomes controlled by translational diffusion.

The switch to translational diffusion control of termination marks the onset of the gel effect, and it is associated with a critical conversion, X_{crit} . Translational diffusion begins to control

propagation at higher conversions.

Martin and Hamielec [45,54] showed that in the diffusion controlled region the termination rate constant could be expressed as a function of the free volume.

$$k_t = k_{t0} (\bar{M}w_{cr}/\bar{M}w)^n \exp\{-A(1/V_F - 1/V_{Fcr})\} \quad (37a)$$

where V_{Fcr} is the critical free volume fraction of solution at the onset of diffusion control.

$\bar{M}w_{cr}$ is the cumulative weight-average molecular weight of the copolymer at V_{Fcr} .

$\bar{M}w$ is the cumulative weight-average molecular weight at $V_F > V_{Fcr}$ for conversions above the onset of diffusion control.

A is an adjustable parameter which determines the rate at which k_t falls off with decreasing volume.

$$\begin{aligned} \text{and } V_F = & (0.025 + \alpha_p(T-T_g)) \phi_p + (0.025 + \alpha_A(T-T_{ga})) \phi_a \\ & + (0.025 + \alpha_b(T-T_{gb})) \phi_b \end{aligned} \quad (37b)$$

where α_j is the difference in the thermal expansion coefficient above and below the glass transition temperature T_g and ϕ_j is the volume fraction of component j in the solution.

Eq. (37c) was given for diffusion controlled propagation reactions.

$$k_{ij} = k_{ijo} \exp\{-B(1/V_F - 1/V_{Fcr})\} \quad (37c)$$

where k_{ijo} is the chemically controlled propagation constant

B is an adjustable parameter which determines the rate at which k_{ij} falls off with decreasing free volume.

These equations predict the change in the termination and propagation constants as the reactions proceeds. They thus take into account the commonly observed autoacceleration or gel effect.

Copolymer Composition

The ultimate properties of a copolymer will depend directly on its composition. Therefore, prediction and control of this composition is important for producing useful copolymer products. The copolymer composition depends on the relative rates of reaction of the monomers involved. Extensive studies with copolymers in bulk and solution have led to the development of the copolymer composition equation for a two monomer system which is presented in Odian's text [1].

$$\frac{d[M_a]}{d[M_b]} = \frac{[M_a] (r_a[M_a] + [M_b])}{[M_b] ([M_a] + r_b[M_b])} \quad (38)$$

This can be rewritten in terms of instantaneous fractions of monomer in both the reaction mixture (f_i) and the copolymer (F_i) by defining

$$f_a = 1 - f_b = [M_a]/([M_a] + [M_b]) \quad (39)$$

$$F_a = 1 - F_b = d[M_a]/(d[M_a] + d[M_b]) \quad (40)$$

and substituting these expressions in eq. (38) to obtain eq. (41).

$$F_a = \frac{r_a f_a^2 + f_a f_b}{r_a f_a^2 + 2f_a f_b + r_b f_b^2} \quad (41)$$

Copolymerization becomes somewhat more complicated when carried out in emulsion systems. The general reaction scheme along with corresponding rate equations for an emulsion copolymerization of two monomers is shown in Table 1. Five basic assumptions have been made in developing this scheme of reactions: (i) polymer particles contain at most one radical; (ii) only monomer radicals can desorb from and reenter into the particles; (iii) no discrimination is made between radicals with or without an initiator fragment on their end; (iv) instantaneous termination occurs when another radical enters a particle which already contains a radical; (v) propagation, termination, and chain transfer reactions in the water phase can be neglected from a kinetic point of view. Assumption (v) is probably not valid for emulsion copolymer systems which involve water-soluble acid monomers.

Schuller [26] has developed equations similar to eqs. (38) - (41) which apply to emulsion copolymer systems. Since many monomers have a wide range of solubilities in water (assuming water is the continuous phase), the concentrations of the monomer in the water will usually be different from the concentrations of monomer in the polymer particles. The resulting copolymer which is generated in each phase will also differ in composition. Schuller developed a copolymer composition

Table 1 - Elementary Reactions and Their Rates [27]

Reaction scheme	Reaction rate
(1) Initiation of radicals in the water phase $I \rightarrow 2I^\bullet_w$	$r_i = 2k_d[I]_w$ (T-1)
(2) Entry of radicals into particles from the water phase	
(i) Instantaneous termination	
$N^\bullet + I^\bullet_w \rightarrow N_0$	$r_{ei} = k_{ei}[I^\bullet_w]_w N^\bullet$ (T-2)
$N^\bullet + M^\bullet_{aw} \rightarrow N_0$	$r_{ia} = k_{ia}[M^\bullet_{aw}]_w N^\bullet$ (T-3)
$N^\bullet + M^\bullet_{bw} \rightarrow N_0$	$r_{ib} = k_{ib}[M^\bullet_{bw}]_w N^\bullet$ (T-4)
(ii) Activation of particle	
$N_0 + I^\bullet_w \rightarrow N_j$	$r_{ei} = k_{ei}[I^\bullet_w]_w N_0$ (T-5)
$N_0 + M^\bullet_{aw} \rightarrow N^\bullet_a$	$r_{ea} = k_{ea}[M^\bullet_{aw}]_w N_0$ (T-6)
$N_0 + M^\bullet_{bw} \rightarrow N^\bullet_b$	$r_{eb} = k_{eb}[M^\bullet_{bw}]_w N_0$ (T-7)
(3) Initiation reaction in particles	
$I^\bullet_p + M_{ap} \rightarrow M^\bullet_{ap}$	$r_{ia} = k_{ia}[M_a]_p N_j$ (T-8)
$I^\bullet_p + M_{bp} \rightarrow M^\bullet_{bp}$	$r_{ib} = k_{ib}[M_b]_p N_j$ (T-9)
(4) Propagation reaction in particles	
$P^\bullet_{ap} + M_{ap} \rightarrow P^\bullet_{ap}$	$r_{paa} = k_{paa}[M_a]_p N^\bullet_a$ (T-10)
$P^\bullet_{bp} + M_{ap} \rightarrow P^\bullet_{bp}$	$r_{pba} = k_{pba}[M_a]_p N^\bullet_b$ (T-11)
$P^\bullet_{ap} + M_{bp} \rightarrow P^\bullet_{ap}$	$r_{pab} = k_{pab}[M_b]_p N^\bullet_a$ (T-13)
$P^\bullet_{bp} + M_{bp} \rightarrow P^\bullet_{bp}$	$r_{pbb} = k_{pbb}[M_b]_p N^\bullet_b$ (T-14)
(5) Chain transfer to monomer in particles	
$P^\bullet_{ap} + M_{ap} \rightarrow P + M^\bullet_{ap}$	$r_{faa} = k_{faa}[M_a]_p N^\bullet_a$ (T-15)
$P^\bullet_{bp} + M_{ap} \rightarrow P + M^\bullet_{ap}$	$r_{fba} = k_{fba}[M_a]_p N^\bullet_b$ (T-16)
$P^\bullet_{ap} + M_{bp} \rightarrow P + M^\bullet_{bp}$	$r_{fab} = k_{fab}[M_b]_p N^\bullet_a$ (T-17)
$P^\bullet_{bp} + M_{bp} \rightarrow P + M^\bullet_{bp}$	$r_{fbb} = k_{fbb}[M_b]_p N^\bullet_b$ (T-18)
(6) Desorption of radicals from particles:	
$N_j \rightarrow N_0 + I^\bullet_w$	$r_{di} = k_{di}N_j$ (T-19)
$N^\bullet_a \rightarrow N_0 + M^\bullet_{aw}$	$r_{da} = k_{fa}N^\bullet_a$ (T-20)
$N^\bullet_b \rightarrow N_0 + M^\bullet_{bw}$	$r_{db} = k_{fb}N^\bullet_b$ (T-21)

equation which accounts not only for the distribution of monomers between the two phases, but it also takes into account the monomer/water ratio. Schuller did not, however, account for significant polymerization in the water phase. Distribution coefficients and a term accounting for the monomer/water ratio are defined by,

$$\alpha_o = [M_a]'/[M_b]'' , \quad \beta_o = [M_b]'/[M_b]'' \quad \mathcal{J} = V'/V''$$

where the superscript (') denotes the particle or oil phase and superscript (') denotes the water phase. The copolymer composition equation is then written in terms of monomer concentrations, eq. (42), or monomer fractions, eq. (43).

$$\frac{dM_a}{dM_b} = \frac{1 + r_a' [M_a]/[M_b]}{1 + r_b' [M_b]/[M_a]} \quad (42)$$

$$F_a = \frac{r_a' f_a^2 + f_a f_b}{r_a' f_a^2 + 2f_b f_a + r_b' f_b^2} \quad (43)$$

where $r_a' = r_a \left(1 + \frac{1}{\alpha_o \mathcal{J}} \right)$ (44)

$r_b' = r_b \left(1 + \frac{1}{\alpha_o \mathcal{J}} \right)$ (45)

In order to use these equations one needs to know the partition coefficients of each monomer as a function of the overall monomer concentrations.

Emulsion Copolymerization Kinetics

Nomura [27] published rate equations for emulsion copolymerization inside the polymer particles.

$$\text{Monomer A} \quad R_{pa} = -dM_a/dt = k_{paa}[M_a]_p N_a^* + k_{pba}[M_a]_p N_b^* \quad (46)$$

$$\text{Monomer B} \quad R_{pb} = -dM_b/dt = k_{pbb}[M_b]_p N_b^* + k_{pab}[M_b]_p N_a^* \quad (47)$$

$$\text{and} \quad R_{ptot} = R_{pa} + R_{pb} \quad (\text{moles/L} \cdot \text{min}) \quad (48)$$

where N_a^* and N_b^* are the number of particles per cm^3 water containing A and B radicals, respectively. Again, note that equations (46) and (47) do not consider polymerization in the aqueous phase.

Nomura [27] used eq. (49) for the composition of copolymer formed in the particles.

$$\frac{dM_a}{dM_b} = \frac{[M_a]_p (r_a[M_a]_p + [M_b]_p)}{[M_b]_p (r_b[M_b]_p + [M_a]_p)} \quad (49)$$

He also assumed that the change in concentration of A^* and B^* radicals with time is slow when compared to the time scale of the complete reaction.

$$k_{pba}[M_a]_p N_b^* = k_{pab}[M_b]_p N_a^* \quad (50)$$

He then defined an average number of respective radicals per particle.

$$\bar{n}_a = N_a^*/N_T, \quad \bar{n}_b = N_b^*/N_T, \quad \bar{n}_I = N_I^*/N_T$$

and,

$$\bar{n}_t = \frac{(N_a^* + N_b^* + N_I^*)}{N_T} \quad (51)$$

The number of initiator radicals is relatively small so that

$$\bar{n}_t = \bar{n}_a + \bar{n}_b + \bar{n}_I = \bar{n}_a + \bar{n}_b \quad (51')$$

After various algebraic manipulations, copolymerization rates can be written.

$$R_{pa} = [1/(1+A)] (k_{paa}[M_a]_p + k_{pab}[M_b]_p) \bar{n}_t N/N_a \quad (52)$$

$$R_{pb} = [A/(1+A)] (k_{pba}[M_a]_p + k_{pbb}[M_b]_p) \bar{n}_t N/N_a \quad (53)$$

$$\text{where } A = n_b/n_a = (k_{paa}/k_{pbb}) (r_b/r_a) ([M_b]_p/[M_a]_p) \quad (54)$$

Nomura [27] also discusses desorption of radicals from the particles. He presented equations which can be used to calculate the desorption coefficients for radical species A and B. However, in order to calculate these coefficients, various mass transfer, diffusion, and chain transfer constants must be known or estimated a priori. The reader is referred to Nomura's article [27] for details.

Homogeneous Particle Nucleation with Emulsion Copolymerization

Mead [28] has developed equations for the prediction of the polymerization rate in emulsion copolymerization systems with significant homogeneous particle nucleation. His work was based largely on the theory developed by Ugelstad et al. [18] for homogeneous nucleation in homopolymer systems and by Nomura [27] for emulsion copolymerization kinetics. The basic reaction scheme is the same as that of Nomura as described in the previous section. As noted earlier, the total number of oligomer radicals for homopolymerization was described by eq. (24).

$$R_{\text{tot}} = \sum_{j=1}^{j_{\text{cr}}-1} R_j \quad (24)$$

This same relationship may be applied to a copolymer system to give eq. (24').

$$R_{\text{tot}} = \sum_{j=1}^{j_{\text{cr}}-1} R_j = [M_a^*]_w + [M_b^*]_w \quad (24')$$

Mead then assumed that the probability of an oligomer radical having an A* or B* end is independent of the chain length. The ratio of B* radicals to A* radicals in the aqueous phase can then be defined as

$$A_w = [M_b^*]_w / [M_a^*]_w = k_{\text{pab}}[M_b]_w / k_{\text{pba}}[M_a]_w \quad (55)$$

and $R_{1a} = R_1 / (1 + A_w), \quad R_{1b} = A_w R_1 / (1 + A_w) \quad (56)$

where R_1 refers to an oligomer radical with one monomer unit attached. Mead then derived the total rate of propagation of R_1 to R_2 as given by eq. (57).

$$R_{ptot} = \frac{R_1}{1+A_w} [(k_{paa} + A_w k_{pba}) [M_a]_w + (k_{pab} + A_w k_{pbb}) [M_b]_w] \quad (57)$$

Primary particle formation occurs when oligomers reach a critical length j_{cr} as described by Ugelstad [18]. Mead used this same concept to derive an expression for the rate of formation of primary particles of length j_{cr} by homogeneous nucleation for emulsion copolymerization. This expression also includes a term for flocculation of primary particles onto latex particles eq. (58).

$$\frac{dN_1}{dt} = \begin{array}{ll} \text{rate of formation} & \text{rate of flocculation of} \\ \text{of oligomers of} & \text{primary particles onto} \\ \text{length } j_{cr} & \text{latex particles} \end{array}$$

$$\frac{dN_1}{dt} = \frac{RK_i + \bar{k}_{des} N_p \bar{n} / N_a}{[1 + \bar{k}_t N_p / KM + \bar{k}_{tw} R_{tot} / KM] j_{cr-1}} - k_{NS} N_p N_1 \quad (58)$$

$$\text{where } KM = \{ (k_{paa} + A_w k_{pba}) [M_a]_w + (k_{pab} + A_w k_{pbb}) [M_b]_w \} / (1 + A_w) \quad (59)$$

k_{NS} = rate coefficient for capture of primary particle by latex particles

N_p = number of latex particles

N_1 = number of primary particles

The term KM accounts for the copolymerization of the two monomers. The assumption by Nomura [27] that propagation and chain transfer in the water phase is negligible applies to eq. (58). This assumption may not be valid for systems in which the monomer(s) have a high degree of water-solubility (i.e. AA, MAA, etc.).

These equations developed by Mead assume that primary particles necessarily form when the oligomer chain length j reaches j_{cr} . This assumption should lead to a good estimate for the number of primary particles formed. However, particles may form in the aqueous phase with initial length $j < j_{cr}$ or $j > j_{cr}$. Therefore, further development of these equations is necessary in order to more completely describe the homogeneous nucleation of primary particles in a copolymer reaction system.

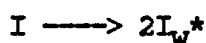
Emulsion Copolymerization with Carboxylic Acid

The complexity of the copolymerization reaction scheme was shown to increase when performed in emulsion systems (Table 1). The complexity is further increased when a carboxylic acid monomer is used. The reaction becomes more like that of a terpolymerization than a copolymerization since both the dissociated and associated acid species must be considered. A detailed reaction scheme for this type of system is shown in Table 2.

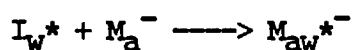
The only attempts to calculate the compositions of the aqueous phase oligomer radicals for carboxylated styrene copolymer systems were

Table 2 - Total Reaction Scheme for Emulsion Copolymerization with a Carboxylic Acid (Monomer a)

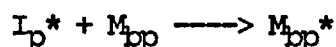
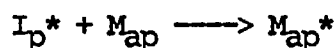
(1) Initiation of radicals in the water phase



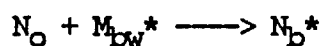
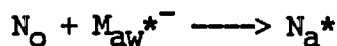
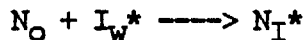
(2) Initiation of monomer (ionized and unionized) in the water phase



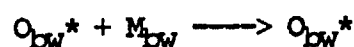
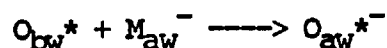
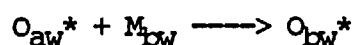
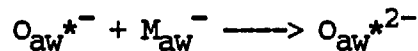
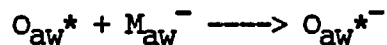
(3) Initiation of monomer in the particles



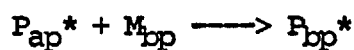
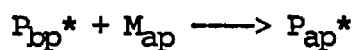
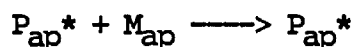
(4) Activation of a particle



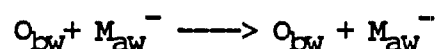
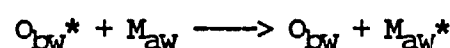
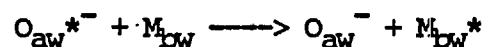
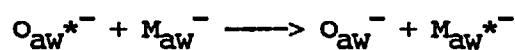
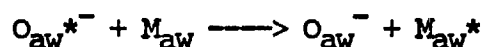
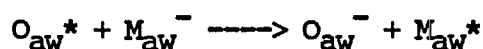
(5) Propagation in the water phase



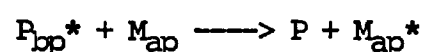
(6) Propagation in the particle



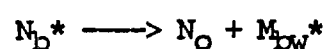
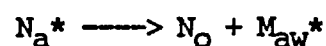
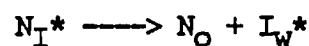
(7) Chain transfer to monomer in the water phase



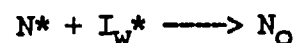
(8) Chain transfer to monomer in the particles

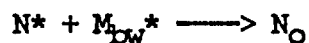
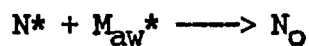


(9) Desorption of radicals from particles

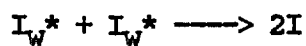


(10) Instantaneous termination in the particles





(11) Termination in the water phase



Dead Polymer



Nomenclature for Table 2

I - initiator

M_{ij} - monomer $i=a,b$ $j=p,w$

N_0 - number of particles with zero radicals

N_i - number of particles with i radicals
 $i = I, a, b$

O_{ij} - oligomer $i=a,b$ $j=w$

P_{ij} - polymer $i=a,b$ $j=p$

Subscripts

a - acid monomer

b - non-acid monomer

i - initiator

p - particle

w - water

Superscript

'-' - ionized species
(dissociated acid)

made by Sakota and Okaya [29]. They considered the particular reaction of undissociated AA, dissociated AA, and styrene. These workers list the following equations to describe the partition and dissociation equilibrium in acid polymerization systems.

$$K = [H^+]_w[A^-]_w/[HA]_w \quad (60)$$

$$[Na^+]_w + [H^+]_w = [OH^-]_w + [A^-]_w \quad (61)$$

$$\delta = [HA]_s/[HA]_w \quad (62)$$

$$C = ([HA]_w + [A^-]_w)/V_w + [HA]_s/V_s \quad (63)$$

where K , δ , C , V_s , and V_w are the dissociation constant of AA, the partition coefficient of AA between styrene and water, the moles of total AA in the polymerization system, the volume of styrene, and the volume of the aqueous phase in the polymerization system, respectively. The symbols HA , A^- , $[\]_s$, and $[\]_w$ represent undissociated AA, dissociated AA, the concentration in styrene, and concentration in the aqueous phase, respectively.

Sakota and Okaya [29] reveal the relationship of pH to degree of neutralization (DN) for AA in Figure 1. Plots of pH versus DN for AA and MAA monomers, and AA polymer obtained in our laboratory are shown in Figures 2 - 4 for comparison. AA polymer is a somewhat weaker acid than AA monomer. When the degree of neutralization is zero, $[H^+]_w$ is much higher than $[OH^-]_w$. Eq. (61) then becomes eq. (64) and the concentration of carboxylic monomer can be calculated from eqs. (60), (62), (63), and (64).

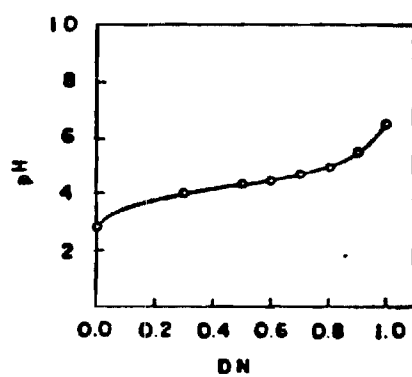


Fig. 1 Relationship between pH of polymerization system and degree of neutralization of carboxylic monomer: DN = degree of neutralization of AA. Formulation for polymerization system, in g: water/AA/ NaHCO_3 /SDS/ K_2SO_4 = 100/5/variable/0.05/0.85. [29]

Figure 2

NEUTRALIZATION TITRATION OF ACRYLIC ACID

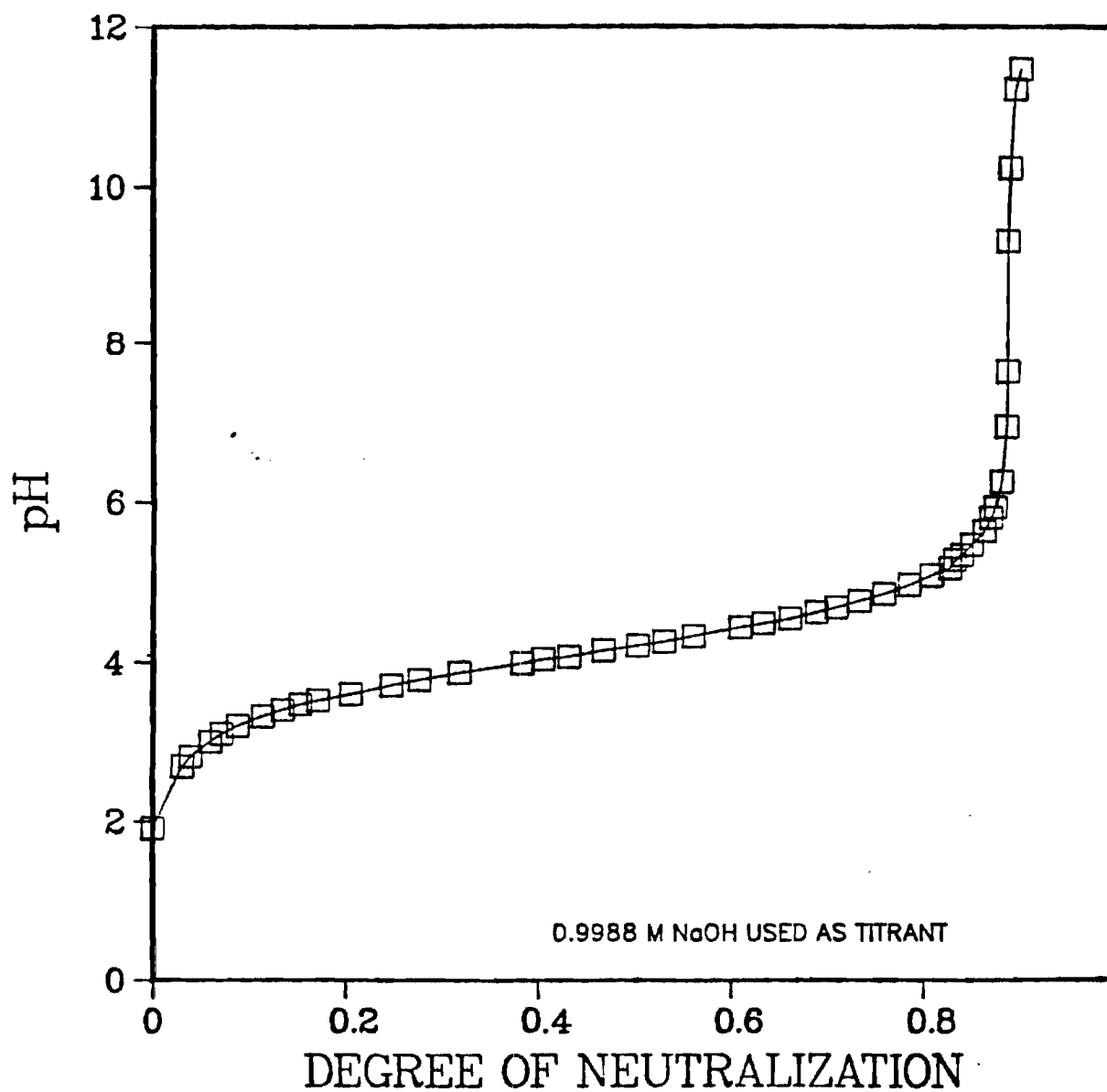


Figure 3

NEUTRALIZATION TITRATION OF AA POLYMER

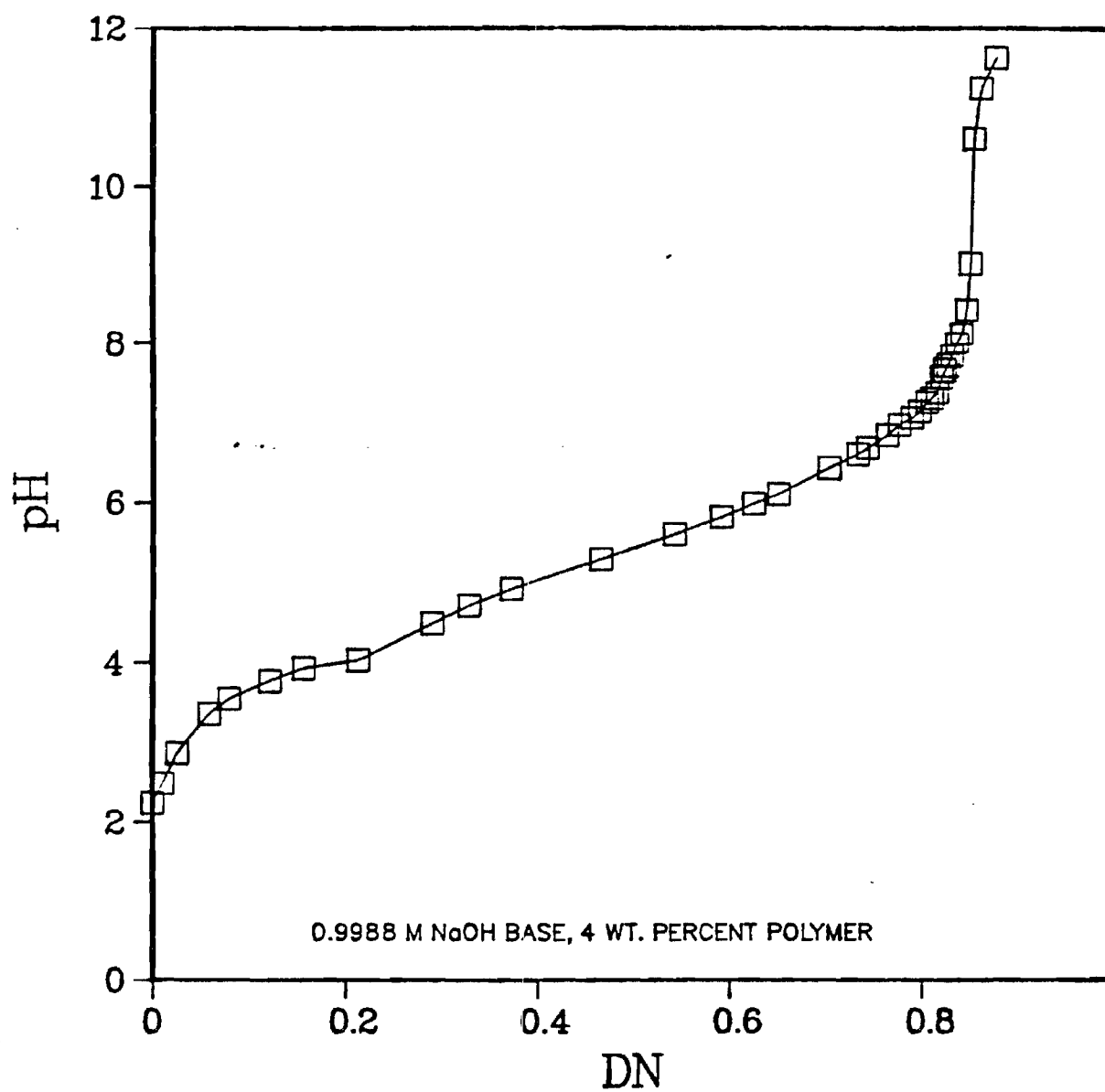
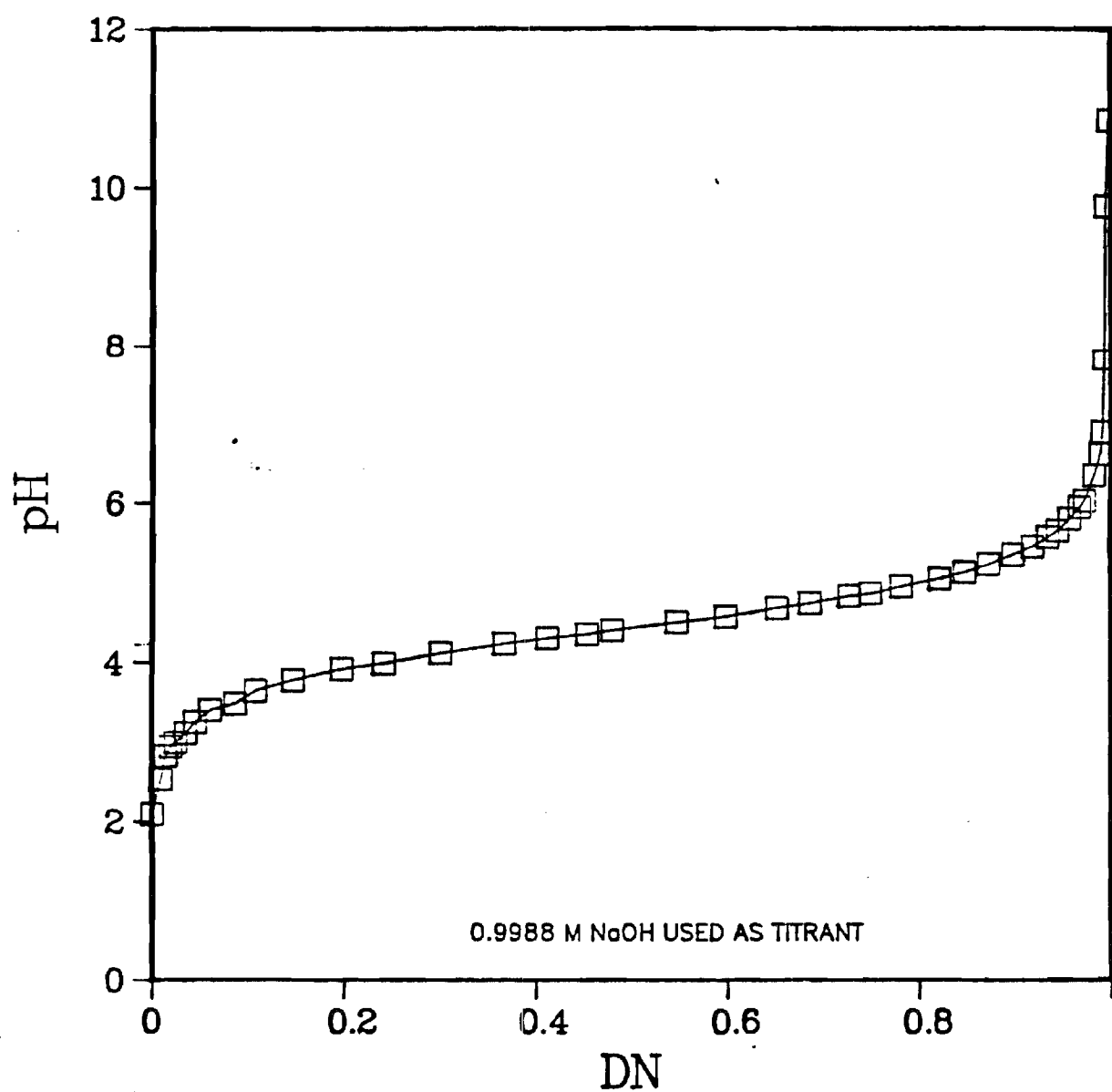


Figure 4

NEUTRALIZATION TITRATION OF MAA



$$[\text{H}^+]_{\text{w}} = [\text{A}^-]_{\text{w}} \quad (64)$$

When the degree of neutralization is near 1.0, $[\text{Na}^+]_{\text{w}}$ is much greater than $[\text{H}^+]_{\text{w}}$ or $[\text{OH}^-]_{\text{w}}$ such that eq. (61) reduces to eq. (65) and the concentration of carboxylic monomer can be determined from eqs. (62), (63), and (65).

$$[\text{Na}^+]_{\text{w}} = [\text{A}^-]_{\text{w}} \quad (65)$$

Sakota and Okaya used a value of 5.66×10^{-5} for K , and calculated V_{s} and V_{w} by assuming densities for the styrene and water phases to be 0.909 g/cm^3 and 1 g/cm^3 , respectively. The concentrations of undissociated and dissociated AA in the aqueous phase were then obtained.

The values for partition coefficients, δ , were determined experimentally [47] by mixing 100 mL of water with a prescribed amount of carboxylic monomer at 25°C . 100 mL of styrene was added and vigorously stirred. The aqueous phase was separated and titrated with NaOH. A mass balance yielded the amount of acid in the organic (styrene) phase. The values obtained differed somewhat from values reported by Matsumotu and Shimada [30], as shown in Table 3. The reason for these differences is not clear. However, possible differences in experimental procedures could have been a contributing factor.

Table 3 — Acid Monomer Partition Coefficients

Monomer	Sakota and Okaya [29]	Matsumotu and Shimada [30]
AA	0.102	0.175
MAA	1.01	1.94

Sakota and Okaya [29] calculated the composition of the growing radical formed in the aqueous phase at the initial stage of polymerization by using the terpolymerization composition equation presented by Alfrey and Goldfinger [31]. Monomer reactivity ratios for the undissociated AA, dissociated AA, and styrene were calculated from the Q and e values reported by Ito et. al. [32] as shown in Table 4. These calculations apply only during the initial stage of polymerization. Since a dynamic equilibrium between undissociated and dissociated AA occurs at all times, the calculations do not represent the concentration of dissociated and undissociated species on an oligomer or polymer chain. These concentrations depend on the current pH or degree of neutralization of the system.

No quantitative models have as yet been developed to account for the kinetics of emulsion copolymerization of carboxylic acid emulsion systems. The goal of this work is to make advances toward the development of such a kinetic model.

Table 4 - Calculation Results of Monomer Reactivity Ratios [29]

Monomer	Notation	Q	e	Monomer Reactivity Ratio
Undissociated AA	M_a	0.40	0.25	$r_{ab}=3.29$; $r_{ac}=0.308$
Dissociated AA	M_b	0.11	-0.15	$r_{ba} = 0.259$; $r_{bc} = 0.121$
Styrene	M_c	1.00	-0.80	$r_{ca} = 1.08$; $r_{cb} = 5.41$

III. EXPERIMENTAL

Experimental work involving basic free radical homopolymerization, conventional bulk and solution copolymerization, and conventional emulsion polymerization is extensive. Theories involving such reactions have thus been well-established. Polymerization involving carboxylic acid monomers, however, have been studied less extensively and are not as well understood. The following discussion, therefore, will address experimental work relating to homopolymerization and emulsion copolymerization of acids and acid plus styrene systems.

Homopolymerization Studies of Acrylic Acid and Methacrylic Acid.

Free-radical polymerizations of acrylic acid and methacrylic acid have been studied by several workers [2-6,33]. Kinetic information such as reaction rates, propagation and termination constants, activation energies plus various effects of solvents and acid dissociation (pH) on these parameters have been determined through these studies. A variety of initiator systems as well as solvent species were used.

Mishra and Bhadani [33] polymerized acrylic acid (AA) in tetrahydrofuran and in 1,4-dioxane with NO_2 as the initiator. The initial rate of polymerization was found to increase linearly with the monomer concentration and the square root of the initiator concentration. Increases in temperature from 40 - 70°C resulted in

significant increases in reaction rate. Galperina et. al. [2,3] studied the effect of solvent on radical polymerization of AA, MAA, and fluoracrylic acid. Solvents used were water, formamide, and dimethylsulphoxide (DMSO). Again, the initial rates of polymerization were proportional to the first power of the monomer concentration and the one half power of the initiator. The rate, therefore, could be described by the basic kinetic equation for free radical polymerization,

$$R_p = R_i^{1/2} (k_p / k_t)^{1/2} [M] \quad (1)$$

Values for k_p , k_t , and activation energies are reported for a range of temperatures. The reactions in water were carried out at low pH (2.2 and below) so that very little of the acid was dissociated. The monomer concentrations ranged from about 2 to 8 wt. %.

Katchalsky and Blauer [4] studied the kinetics of MAA polymerization in aqueous solution using hydrogen peroxide as initiator. Buffers were used to maintain a constant pH. The overall polymerization rate was found to be first order with monomer concentration. First order rate constants (K) were determined over a wide range of initial monomer concentrations and were found to be fairly consistent. The overall rate constants were also determined for a range of initiator concentrations. The constants depended on the $1/2$ power of the initiator concentration.

Katchalsky and Blauer [4] further studied the variation of rate with pH. They noted that the rate decreased as the pH increased from 0.97 to 5.5. (See Table 5.) Above a pH of 5.5 the rate of reaction was negligible. Pinner [5] later attributed the lack of reaction above a pH of 5.5 to the suppressed decomposition of the peroxide initiator. When potassium persulfate was used as initiator, reaction occurred at pH values as high as 13. Blauer [6] later extended his study of the polymerization of MAA to pH 12 using 2,2'-azobisisobutyronitrile as initiator solubilized in water by the addition of 4% (by volume) ethanol. The course of reaction was followed by bromine addition to the unreacted monomer. The dependence of rate on pH (for pH between 4 and 12) is illustrated in Figure 5.

The rate of polymerization decreases sharply up to pH 6-7 as observed in their first study [6]. This is not surprising since the degree of neutralization (and thus the concentration of anions) increases sharply between pH 4 and 5. The rate then slowly increases to a flat maximum at pH 11. This flat maximum indicates that the rate is fairly constant between pH 9-12. Blauer asserts that the dependence of rate of MAA polymerization on the pH suggests that both un-ionized and ionized monomers and radicals do copolymerize.

The reaction rate was observed to increase as the pH decreased in the previous studies of acid homopolymerizations. When HNO_3 and H_2SO_4 were added to lower the pH this trend was observed [4]. Increased rates were also observed when the reaction was run at decreasing pH with no strong acid present. These experimental results suggest that the ionized structure of the acid monomer (as shown below)

TABLE 5 — VARIATION OF RATE WITH pH

pH	$1-a$	$(K \times 10^4) \text{ sec.}^{-1}$	$[K/(1-a)] \times 10^4 \text{ sec.}^{-1}$
0.97 *	1.000	2.28	2.28
0.99 †	1.000	1.55	1.55
2.41 ‡	0.989	1.94	1.96
3.17	0.939	2.01	2.14
3.58	0.858	2.09	2.44
3.58	0.858	1.74	2.03
3.58	0.858	1.97	2.29
3.81	0.780	1.71	2.19
3.97	0.711	1.13	1.59
3.97	0.711	1.09	1.53
4.23	0.574	0.881	1.53
4.23	0.574	0.881	1.53
4.23	0.574	0.902	1.57
4.23	0.574	0.959	1.67
4.23	0.574	0.959	1.67
4.90	0.201	0.327	1.63
4.96	0.201	0.345	1.72
5.26	—	0.058	—

$$K/(1-a) = K_0 = (1.84 \pm 0.08) \times 10^{-4} \text{ sec.}^{-1}$$

* Solution contained nitric acid. Precipitation of the polymer occurs during the polymerization.

† Sulphuric acid solution. Here, too, precipitation of polymer occurs.

‡ From this pH upwards, 0.2 M sodium acetate + hydrochloric acid buffer was used. At pH 3.2 some polymer precipitation still occurs, but at higher pH values the polymerization is fully homogeneous.

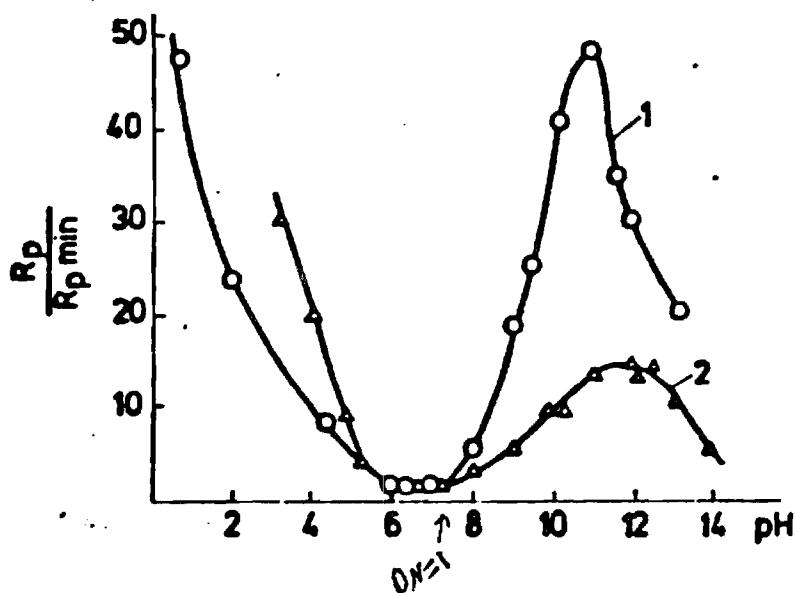
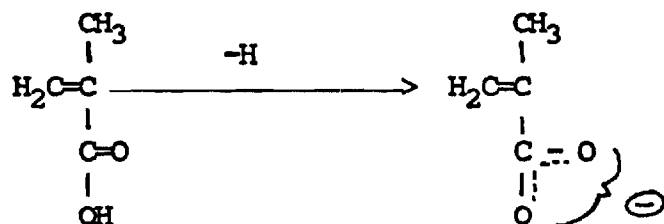


FIG. 1. Relative rates of polymerization vs pH adjusted by an addition of NaOH for MAA (1) and AA (2) at 60°C.

Curve 1: $R_p \text{ min} \times 10^5 = 0.115 \text{ M s}^{-1}$, $[\text{MAA}] = 0.92 \text{ M}$, $[\text{AIBN}] = 5 \times 10^{-4} \text{ M}$, Curve 2: $R_p \text{ min} \times 10^5 = 0.43 \text{ M s}^{-1}$, $[\text{AA}] = 1.2 \text{ M}$, $[\text{AIBN}] = 5 \times 10^{-3} \text{ M}$. Replotted from Fig. 1 of Ref. 23.

K. Plochocka, J. Macromol. Sci. - Rev. Macromol. Chem.
C20(1), 67, (1981)



does not take part in free radical polymerization as actively as the undissociated acid form. These results would further suggest that the ionized acid monomer and ionized radical are even less likely to react with each other due to the increased electronegative repulsion. It should also be noted that addition of HCl slowed the reaction [4] despite lowering the pH. Addition of NaCl to the buffer also decreased the rate. The chloride ion was apparently responsible for the decreased rate when HCl or NaCl were added. An explanation for this behavior was not suggested.

Copolymerization Studies of Hydrophobic Monomers (i.e. Styrene) with Carboxylic Acid Monomers

A significant amount of literature exists for emulsion copolymers containing carboxyl groups. Basic studies of the potentiometric titration behavior of polyacids have been performed by Mandel [34], Leyte and Mandel [35], and Gregor and Frederick [36]. Potentiometric and conductometric studies of copolymer latex systems containing acid monomers copolymerized with a more hydrophobic monomer such as styrene have been performed by a variety of workers including Muroi [37],

Vijayendran [38], Sakota and Okaya [39], Egusa and Makuuchi [40], Ceska [41,42], Fordyce and Ham [43], and Gasper and Tan [44]. Most of these titration studies were aimed at determining the distribution of the acid groups between the aqueous phase, particle surface, and particle interior and the effects of these distributions on the rate of polymerization, particle stability, and particle generation.

The most frequently studied acid monomers copolymerized with styrene (or other hydrophobic monomers) are itaconic acid (IA), AA, and MAA, listed in order of increasing hydrophobic nature. The partition coefficients as reported by Matsumoto and Shimada [30], are 0.012, 0.175, and 1.94, respectively. They did not account for variation of these values with monomer concentration. The amount of acid found buried inside the particle core increases with the hydrophobicity of the monomer [37,38,40,44,45]. Hydrophobic monomers diffuse into the particle, polymerize, and become a part of the particle core more easily than hydrophilic monomers. Hydrophilic acid monomers such as IA must be carried to the particle surface by oligomeric radicals which have polymerized in the aqueous phase [41]. Very little IA monomer becomes incorporated within the particle core. The concentration of IA in the free aqueous phase is, therefore, greater than MAA when equal amounts are charged. The incorporation of AA into the particle core is intermediate between IA and MAA [37,38,40,44,45].

Ceska copolymerized IA, AA, and MAA with styrene in separate reactions. Copolymerization rates were found to increase in the presence of carboxylic monomers in the order $IA < AA < MAA$ [17,18]. The rate increased as the hydrophobicity of the monomer increased.

This relationship between the reaction rate and the hydrophobicity of the acid monomer may be due to the role of the acid monomer in particle nucleation. Ceska [41] stated that particle nucleation in these comonomer systems begins in the aqueous phase by the generation of oligomers which agglomerate and nucleate after growing to a critical chain length, i.e. homogeneous nucleation. These particles become swollen with styrene monomer and stabilized by carboxyl and sulfate moieties. The reaction rate increases as more particles are generated and stabilized.

The fact that the rate of reaction increased with increasing hydrophobicity of the acid monomer implies that the more hydrophobic acid monomers become incorporated into the particles more rapidly than the more hydrophilic acid monomers. Particle stabilization is enhanced by the carboxyl groups in these acid monomers. Therefore, the incorporation of these carboxyl groups from the more hydrophobic acid into the particles helps stabilize these particles earlier in the reaction resulting in less flocculation and thus a larger number of stabilized particles than when a less hydrophobic acid is used. The polymerization rate will also increase when the more hydrophobic acid is used due to the larger number of particles in the reaction medium. Ceska measured the rate, but he did not report measurements for the number of particles generated with each acid monomer. Therefore, the above conclusion is not proven directly by Ceska's data.

Egusa [46] performed experiments similar to those of Ceska by copolymerizing IA, AA, and MAA with styrene. Egusa, however, used radiation instead of persulfate to initiate the reaction to avoid the

production of additional acid groups from persulfate species. He observed an increase in copolymerization rates which agreed with that reported by Ceska, $IA < AA < MAA$. However, Egusa noticed essentially no difference in the number of particles produced when different acid monomers were used. He postulated that particle nuclei are generated from soap micelles when initiated with radiation instead of forming from water-insoluble oligomers. Therefore, the hydrophobicity does not affect the number of growing particles since the particles do not originate in the aqueous phase. Egusa, therefore, suggested that the increase in copolymerization rate with increasing hydrophobicity of the acid monomer occurs because the bulk hydrophobic monomer, styrene, more easily transfers from the dispersed phase to the polymer particles when in the presence of a molecule which can distribute itself between the oil (styrene) and water phases. A more hydrophobic acid monomer would, therefore, be expected to provide a faster overall rate than a more hydrophilic acid monomer. This is indeed observed, as noted previously, for the copolymerization rate increases with the hydrophobicity of the acid monomer, $IA < AA < MAA$. However, diffusion of monomer to the particles is usually not the limiting step in emulsion reactions involving styrene. Egusa's explanation is, therefore, questionable.

Particle stability and nucleation with carboxylated systems has been studied in detail by Ceska [41,42] and especially by Sakota and Okaya [29,46,47]. It is well understood that most surfactants which are effective stabilizers adsorb onto the surface of a particle and form a negatively charged hydrophilic shell around the particle. The

negative charge density at the surface repels other particles as they approach thus minimizing the chance of agglomeration. Carboxyl groups present at the particle surface can function in the same capacity. Ceska [42] points out that these chemically bound carboxyl groups are often more effective stabilizers because the negative charge is not as free to move around the surface as it is with adsorbed surfactant molecules. Ceska [42] demonstrated through experiments that stabilization of small particles using carboxylated systems can effectively be achieved with much less surfactant than is needed for most non-carboxylated systems. Ceska [41] and Sakota and Okaya [46] showed in further experiments that stable systems can be achieved with surfactant-free emulsion copolymerization systems when carboxylic monomers are used. Particle stability increases as the concentration of carboxyl groups at the surface increases due to the increase in charge density. Since AA is more hydrophilic than MAA, AA creates a more acidic particle surface than MAA, for it concentrates at the particle surface. It is, therefore, more effective in producing the stabilizing negative charge density at the surface of the particle.

Particle Nucleation

A large number of stable particles form in acid-styrene systems with no emulsifier present. Particle nucleation in systems which contain little or no surfactant cannot occur in micelles since micelles would not be present. Particle formation is, therefore, attributed to combination and nucleation of highly carboxylated oligomers formed in the aqueous phase [17,29,42,46,48].

Initial studies by Sakota and Okaya [29] showed that the number of particles and thus the polymerization rate was greatly dependent on the degree of neutralization of the carboxylic acid. A maximum in both respects was achieved at a degree of neutralization of 0.8 (Figure 7). Sakota and Okaya [29] explain that the hydrophilic nature of the growing radical changes considerably with DN, because $r_{cb} \gg r_{ca}$ (see Table 4). Naturally, as DN increases, the pH increases and the concentration of dissociated acid increases while the concentration of undissociated acid decreases. Styrene reacts more with itself when in the presence of dissociated acid than is the case when undissociated acid is present. Thus the water phase radicals are comprised of more styrene units causing the oligomeric radical to become more hydrophobic at higher pH. A relatively hydrophobic oligomeric radical is more likely to precipitate from the aqueous phase at a shorter chain length j than a relatively hydrophilic radical. Therefore, as the DN increases, the value for j_{cr} will decrease and the number of particles will increase thus increasing the rate of reaction. However, as the DN increases the concentration of dissociated acid (which is less reactive than the undissociated acid) increases causing the average propagation constant to decrease. A balance between these two opposing effects on the reaction rate apparently occurs at a DN of 0.8. Subsequent experimental studies by Sakota and Okaya were performed at this degree of neutralization.

Sakota and Okaya [46] performed experiments to determine the effect of surfactant concentration on the number of particles using AA and styrene monomers. The concentration of sodium dodecyl sulfate

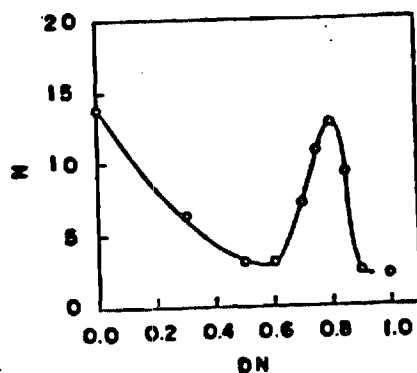


Fig. 6 Change in number of particles in the polymerization system with degree of neutralization of carboxylic monomer: N = number of particles in the polymerization system, $\times 10^{15}$; DN = degree of neutralization of AA. [29]

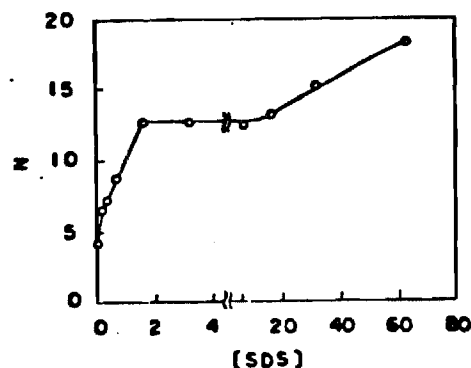


Fig. 7. Change in number of particles in the polymerization system with soap concentration: N = number of particles in the polymerization system $\times 10^{15}$; $[SDS]$ = concentration of SDS, in mmole/l. [46]

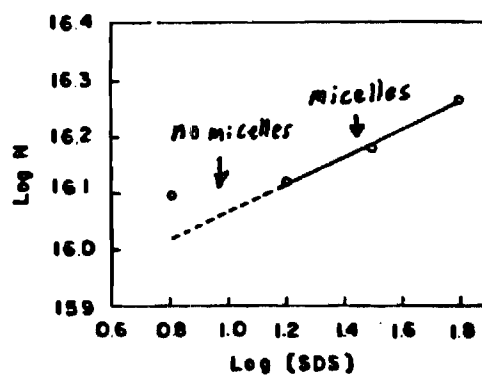


Fig. 8 Relationship between logarithms of number of particles in the polymerization system and SDS concentration: N = number of particles in the polymerization system $\times 10^{15}$; $[SDS]$ = concentration of SDS, in mmole/l. [46]

(SDS) was varied from 0.0 to 63.0 mmol/L. (See Figure 7). The large number of particles formed in the absence of SDS indicates that particles were formed by precipitation of growing radicals generated in the aqueous phase (and possibly in monomer droplets as well, though no distinction was made between these two loci). The number of particles increased linearly with SDS concentration up to 1.60 mmol/L irregardless of the absence or presence of SDS micelles. The surfactant functioned mainly by stabilizing the precipitating particles in this SDS concentration range. When the SDS concentration was increased from 1.6 to 6.4, the number of particles remained relatively constant which indicated that micelles did not play an important role in nucleation for SDS concentrations up to 6.4 mmol/L. The particle number did not continue to increase because the SDS apparently was above the critical concentration needed to stabilize the precipitating particles.

When the SDS concentration was increased above 6.4 mmol/L, the number of particles began to increase again, and it was at this point that micelles began to play a significant role in particle formation despite the fact that the CMC for SDS is reported in the literature to be 9.0 mmol/L. The relationship between the number of particles and the SDS concentration in this high concentration region is linear when plotted on a log plot (Figure 8). The linear relation is directionally consistent with the Smith-Ewart theory although the slope of the curve is somewhat different at a value of approximately 0.25 as opposed to 0.6 by the Smith-Ewart theory.

Sakota and Okaya [46] calculated the maximum degree of polymerization using Fitch and Tsai's equations for L and DP_{max} . The approximate result was about four times larger than DP_{max} values reported for poly(methylmethacrylate) and poly(vinyl acetate) as shown below.

	AA, Styrene	P(MMA)	P(VA)
DP_{max} (calculated)	230	65	50

This result is not surprising since the oligomeric radicals in the system containing acid monomers are much more hydrophilic.

Sakota and Okaya [46] also varied the initiator concentrations and found that the number of particles increased in a linear fashion. The number of particles became independent of concentration at high levels of potassium persulfate. This fact was attributed to the increased probability of termination between radicals occurring in the aqueous phase, although the additional electrolyte could also have caused particle flocculation.

Variation of the styrene concentration had no effect on the number of particles probably because the styrene was always above its solubility limit. Therefore, the concentration of styrene in the aqueous phase did not change significantly. It is not clear how styrene effects particle formation when it is added to carboxylated systems in concentrations below its solubility limit.

IV. PROPOSED WORK

The goals of this work will be to develop a better understanding of emulsion copolymerization of carboxylic acid monomers with more conventional hydrophobic monomers. Studies will involve both homopolymerization and copolymerization reactions. Topics to be studied will include the effects of monomer concentration, pH, temperature, monomer partition between aqueous and particle phases, monomer/water ratio, and particle nucleation on the reaction rate. Compositions of the oligomer and copolymer will also be determined. An ultimate goal will be to develop a quantitative model to describe the overall kinetics.

A unique problem associated with reaction systems involving a carboxylic acid monomer plus a hydrophobic monomer is that the reaction involves two monomers, yet three reaction species; the undissociated acid, the dissociated acid, and the hydrophobic monomer. Therefore, terpolymerization composition and kinetic equations should theoretically be used. Terpolymerization equations require many rate constants k_{ij} ($i, j = a, b, c$) which are not known and can only be estimated by the Q-e scheme which is not always a reliable method. Blauer [50] indicated that the interaction constants of the active end-group of a charged macromolecule are expected to be dependent on the degree of ionization of the polymer radical. He states that assignment of a single 'e' value to ionized AA or MAA and the subsequent calculation of copolymerization parameters remains suspect.

Sakota and Okaya [29], as discussed previously, attempted to calculate the terpolymer composition using the terpolymer composition equation of Alfrey and Goldfinger [31] and the reactivity ratios obtained from the Q-e scheme. They calculated the composition of the three species at the initial stage of reaction. Results obtained from this method, however, can not predict the copolymer composition for times beyond the very initial stages of reaction because the equilibrium between undissociated and dissociated species continues even after incorporation of the monomer into a chain. Therefore, unlike conventional terpolymerization where the composition of all three species in an oligomer (or polymer) chain is set once the monomers have reacted to form the chain, the acid and its anion may interchange their identities (positions) on the chain via the dynamic equilibrium process.

Figure 9 shows how the charge on a carboxyl branch of an oligomer radical may shift to different constituents on the chain while the overall concentration of undissociated and dissociated carboxyl groups remains constant. This same dynamic equilibrium exists for a dead polymer chain. The average overall concentration of undissociated and dissociated species remains relatively constant for a given set of conditions. However, the particular location of each species on a chain does not. Moreover, the addition of a neutralizing agent or additional acid or base which changes the pH will result in a change in the overall concentration of undissociated and dissociated acid species. Therefore, the compositions predicted by the terpolymerization equation of Alfrey and Goldfinger [31] may not apply

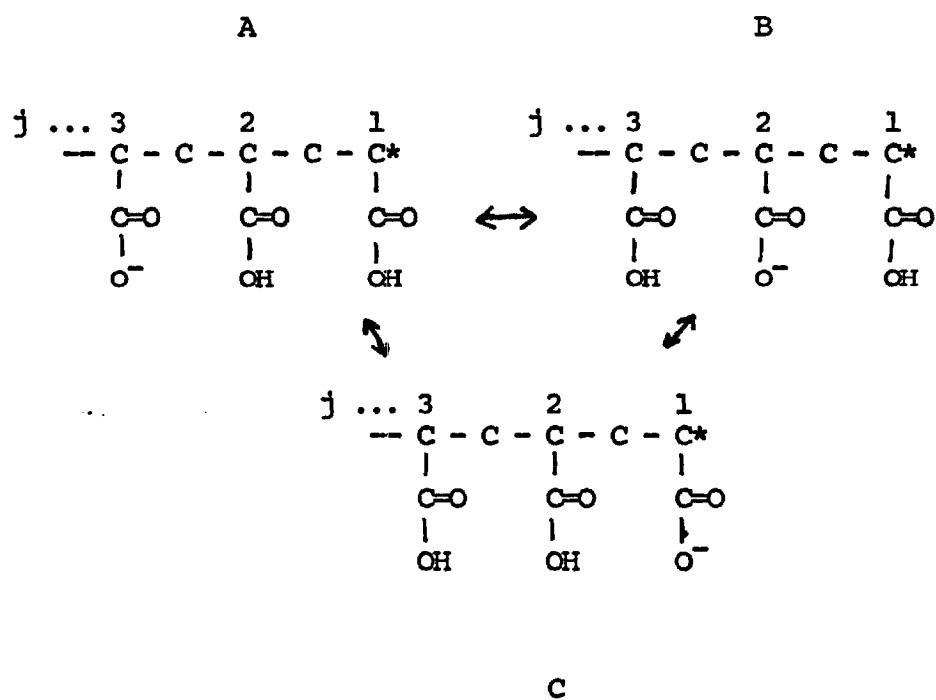


Figure 9 - Oligomeric radicals with an anionic charge on a constituent along the chain.

since the species at a particular location on a chain may change its identity.

The concept of terpolymerization in the aqueous phase reaction medium is certainly valid since the reactivities of undissociated acid, dissociated acid, and hydrophobic monomer all differ, and the relative amounts of each species affects the overall rate of polymerization. Experimental data by Katchalsky and Blauer [4] and Pinner [5] support this assertion. Their data show that the overall rate decreases as the concentration of dissociated acid increases (pH increases).

The question then arises as to how the location of the anion with respect to the free radical affects the polymerization rate. If the anion indeed decreases the reactivity when the anion is located on the reactive end of the chain, then species A, B, and C in Figure 5 probably exhibit the following relative reactivity $A > B > C$. Using a statistical approach and knowing the amounts of undissociated and dissociated acid units from the pH, one could probably estimate the number of anionic groups at positions 1, 2, 3,..., j as shown in Figure 5. One could then write equations which would include rate constants for each type of radical species 1, 2, 3,..., j based on the position of the anion with respect to the free radical carbon. The overall rate expression would then depend on j reacting species where j is the number of possible positions along an oligomer chain to which an anion species may be attached. This type of system is very complex and rate constants for each species would be almost impossible to determine.

A more feasible approach is to look again at a copolymerization scheme in which only r_a avg and r_b need to be determined. r_a avg in this case actually represents the reactivity of two species, the undissociated acid and its anion. These species are directly related by a measurable parameter, α (or pH). This fact suggests that r_a avg should be a function of pH. The problem then is to determine the overall reactivity of the acid as a function of the relative amount of undissociated acid and anion species (i.e. as a function of the pH).

An empirical approach to this problem is to run reactions at various pH values and calculate corresponding r_a avg and r_b values by the method outlined by Nishida [49]. The relation of r_a avg to pH can then be correlated for each monomer. Calculations for the aqueous phase reactions can then be treated as regular copolymerization reactions since the effect of pH is included in the r_a avg value as well as the k_p (acid) value. The basic copolymer equation will give the relative amount of acid to hydrophobic monomer species. Distinction between the undissociated and dissociated acid units in the polymer chain can not be predicted directly from the terpolymer composition equations since their location on the chain is not constant. However, once a polymer chain has terminated, the properties of that polymer should depend only on the average concentration of the undissociated and anion species and not the position of the anion relative to the chain end as was the case with the reacting oligomer radical. Therefore, the pH alone should account for any distinction between the overall concentration of acid and anion species and the relative properties of the copolymer.

Proposed Kinetic Models

A model to predict the overall copolymerization kinetics for emulsion systems in which highly water-soluble acid monomer is used must account for reaction in both water and particle phases. Previous models for emulsion copolymerization only considered reaction in the particle phase. The overall rate equation should have the general form:

$$R_p \text{ tot} = (R_p)_{\text{aq}} + (R_{\text{pa}})_p + (R_{\text{pb}})_p \quad (66)$$

Eqs. (52) and (53) developed by Nomura may be used to predict the rates of reaction in the latex particles, $(R_{\text{pa}})_p$ and $(R_{\text{pb}})_p$. These equations have been shown to work well in emulsion systems in which most of the conversion resulted from reaction inside the particles.

Eqs. (52) and (53) do not account for propagation, termination, and chain transfer in the aqueous phase. An additional expression, $(R_p)_{\text{aq}}$ must be developed to account for these aqueous phase reactions.

Reaction in the aqueous phase is technically a solution terpolymerization involving undissociated acid, dissociated acid, and the base monomer. The terpolymerization reaction scheme involves a large number of rate constants k_{ij} , and it is more difficult to use than the copolymer scheme. The terpolymerization scheme for these acid/styrene systems is not useful for predicting the composition of the polymer since two of the reacting species (the acid and anion) are in equilibrium and do not retain their same identity on the chain at

all times. The position of the acid monomer unit as a whole, however, is stable so that a scheme which predicts copolymerization composition is most applicable. Therefore, the terpolymerization scheme will not be used initially. A more simplified approach which accounts for the effects of all three monomeric species, yet utilizes copolymerization equations will be pursued. This approach is discussed below.

The basic copolymer equation based on diffusion controlled termination may be applied if the system of three monomeric species is reduced to two primary monomer species, carboxylic acid (A) and base monomer (B). (This equation does not account for chain transfer in the aqueous phase.)

$$(R_p)_{aq} = \frac{R_i^{1/2} (r_A[M_A]_w^2 + 2[M_A]_w[M_B]_w + r_B[M_B]_w^2)}{(2k_t(AB))^{1/2} \{r_A[M_A]_w/k_{AA} + r_B[M_B]_w/k_{BB}\}} \quad (67)$$

$[M_A]$ accounts for the total ^{aq. phase} acid concentration, both undissociated and dissociated forms. Both r_A and k_{AA} depend on the relative amount of undissociated and dissociated species. r_A may be determined experimentally by measuring the reactivity ratios at extreme values of pH and assuming a linear relationship in between. The accuracy of this method can obviously be improved by measuring reactivity ratios at more than two pH values. An alternative method of determining r_A is to use the Q-e method to determine r values for the acid (r_{HA}) and anion (r_{A^-}). r_{HA} and r_{A^-} may be estimated from the Q-e scheme, a method which is not always reliable. It is, however, the best method currently available

since these r values can not be found in the literature. A value of r_A can then be estimated by a simple weighted average of the values for r_{HA} and r_{A^-} based on the value of α . (r_A then is the same as r_a avg discussed previously and r_B is equivalent to r_p .)

$$r_A = (1 - \alpha) r_{HA} + \alpha r_{A^-} \quad (68)$$

Once these reactivity ratios have been determined, k_{AA} may be predicted as a function of pH (a measurable variable). As noted earlier, the apparent "homopolymerization" of a carboxylic acid monomer is actually a copolymerization of the acid and anion species. The copolymerization equation (37) above may be applied where now A is replaced by HA (acid) and B is replaced by A^- (anion). The monomer concentrations can be rewritten in terms of the total monomer concentration at time t by:

$$[M_A] = (1 - \alpha) [M_t] \quad (69)$$

$$[M_{A^-}] = \alpha [M_t] \quad (70)$$

Then assuming that $\beta = \alpha$ and $k_{p,2} = k_{p,3}$ as Pinner did when using the copolymerization equation based on chemical controlled termination, the following expression can be derived assuming diffusion controlled termination.

$$R_{p \text{ acid}} = k_{AA} (R_i/2k_t)^{1/2} [M_t] \quad (71)$$

$$\text{where } k_{AA} = \frac{r_{HA} (1-\alpha)^2 + 2\alpha(1-\alpha) + (r_A)\alpha^2}{r_{HA} (1-\alpha)/k_{p,HA} + (r_A)\alpha/k_{p,A^-}} \quad (72)$$

Determination of $k_{p,HA}$ and k_{p,A^-} may be obtained from homopolymerization reactions at low and high DN.

Use of these expressions does require that three reactivity ratios be evaluated as well as three propagation constants. However, this approach reduces the ultimate problem to that of a copolymerization while still accounting for the reaction of three distinct species. A copolymerization reaction scheme is much easier to handle, especially when prediction of copolymer composition is desired.

Values of N , particle number, will be obtained from known concentrations of seed particles or directly from experimental measurements if no seed latex is utilized. If the particle number changes significantly throughout the conversion period despite the presence of seed particles (i.e. if all primary particles formed in the aqueous phase do not flocculate onto the seed particles), then a theoretical expression will have to be developed and included in the overall kinetic model to predict the primary homogeneous nucleation of particles.

The theoretical prediction of primary particle number for homogeneous nucleation may possibly be approached by using the relation of Ugelstad [18] as modified by Mead [28] for copolymerization eq. (58). Instead of assuming steady-state as Mead did for CSTR

studies, the differential equations would be integrated numerically to determine particle number as a function of time. Other modifications to account for particle formation at j other than j_{cr} may also be needed.

The calculational procedure for the overall kinetic model would involve simultaneous integration of all rate expressions as a function of time. After each time step, new monomer concentrations would be calculated for each phase and various parameters would be adjusted. Calculations would proceed until the overall conversion approached unity. Model predictions would be compared to the experimental data.

Proposed Experimental Work

Monomer Selection

Monomers to be used in this study include acrylic acid (AA) and methacrylic acid (MAA). AA and MAA were chosen for several reasons: (i) they are both well described in the literature; (ii) they have similar chemical structures; (iii) they exhibit similar water-phase reaction behavior; but (iv) they exhibit a distinguishable difference in hydrophobicity such that their incorporation into polymer particles will differ; (v) they are not extremely dangerous with which to work; and (vi) they have significant industrial importance. Itaconic acid (IA) due to its high degree of hydrophilicity may also be used in some studies.

Styrene is suggested for the initial bulk phase monomer for the copolymerization studies. It has been studied extensively, and its properties are well-understood both in solution and emulsion. It likewise has significant industrial importance. More hydrophilic monomers such as methyl acrylate may also be used in order to better understand the interactions of the acid and bulk monomers in the aqueous phase.

Homopolymerization Reactions

Homopolymerization reactions of the acid monomer using potassium persulfate as the initiator will be run under a wide range of reaction conditions in order to fully characterize the effects of parameters

such as monomer concentration, temperature, and pH or degree of neutralization (DN). Table 6 lists the conditions for proposed homopolymerizations of AA and MAA. Samples will be collected over time in each reaction and analyzed for conversion. Buffers will probably be necessary for maintaining a constant pH during these reactions. Measurements of pK_a versus temperature will also be made in order to determine the correct amounts of neutralizing agent (NaOH) needed to attain the desired pH in the reaction mixture at the temperature of interest. Initial measurements in the lab suggest that pK_a changes very little with temperature.

Table 6 - Proposed Conditions for Homopolymerization Reactions of AA and MAA

<u>Variable Parameter and Values</u>		<u>Set Parameters</u>
Weight % monomer (based on total sol.)	2%, 4%, 7%, 10%	Temp=85°C, DN = 0
Temperature (°C)	70, 85, 100	Wt. % = 7, DN = 0
	70, 85, 100	Wt. % = 7, DN = 1
DN (approx. pH)	0.0, 0.25, 0.50, 0.75, 1.00 (2.4) (3.9) (4.4) (4.8) (8.0)	Temp.=85°C, Wt. %=7

Emulsion Copolymerization Reactions

Emulsion copolymerization reactions using an acid monomer (AA, MAA) and a hydrophobic monomer (styrene, MA) will be performed to obtain the following information: reaction rates (overall and for individual monomers), particle numbers, reactivity ratios, partition coefficients, critical chain lengths, and oligomer and latex copolymer compositions. The experimental approaches for obtaining this information are outlined in the remainder of this proposal.

(1) Reaction rates - Copolymerization reactions will be run with acid monomers (0 - 10 weight percent based on total monomer) and styrene (and possibly methyl acrylate). Surfactant concentrations will be below the critical micelle concentration to discourage new particle formation. The hydrophobic monomer will be present in concentrations above its solubility limit. Initial reactions will be run in the presence of seed particles of known size and concentration. The particle number for the final latex in several initial runs will be measured to see whether new particles which may form in the aqueous phase are stabilized or whether they coagulate onto the seed particles thus keeping the total concentration of particles constant. Degree of neutralization will be varied from 0 to 1.0 (corresponding to a pH range of approximately 2.2 to 8.0). Samples collected every 5 to 10 minutes will be measured for conversion using gravimetric and GC analysis. Since the pK_A of the acid polymer differs somewhat from that of the monomer, the pH of the reaction mixture may increase slightly during the course of the reaction. If this change is very large, a buffer will have to be added to the reaction mixture.

(2) Particle number - Samples from (1) above may be used to measure particle size and particle size distribution using an HDC. A mass balance may then be used in conjunction with the average particle size to calculate the particle concentration in the latex. Separate unseeded reactions may also be employed to obtain additional data concerning primary particle nucleation as a function of time. Electron microscopy may also be employed for some particle size measurements.

(3) Reactivity ratios - Monomer conversion data obtained from (1) may be used to determine reactivity ratios. Several curve fitting methods are available for obtaining these values. One modification which will be necessary for most of these methods will be to account for the effects of the different monomer concentration in the aqueous and particle phases due to partitioning. This may be accomplished by fitting r_a' and r_b' to the data. Values of r_a and r_b which apply to aqueous phase copolymerization may then be calculated from the fitted r_a' and r_b' values once partition coefficients are obtained. Attempts will be made to calculate reactivity ratios at various values of DN (pH).

(4) Partition coefficients - GC data obtained in (1) may be used directly to back out partition coefficients of the acid and styrene (or MA). A second method of obtaining partition coefficients is to mix styrene with an acid solution of a specified DN (pH) and allow the mixture to attain equilibrium. Samples of the aqueous phase may be analyzed for concentration of each monomer using a GC or by titration of the acid. Partition coefficients may then be calculated for a range of DN (pH) using mass balances.

(5) Critical chain length (j_{cr}) - A small amount of styrene (below its solubility limit) will be reacted with a set amount of acid (4 - 7% based on the total weight of the reaction mixture). The reaction will be run at an intermediate temperature (85°C) and a turbidity measurement of the final sample will be made by a UV light spectrophotometer to detect whether particles are present in the final reaction mixture. The reaction will be repeated using increasing amounts of styrene until particles precipitate from the reaction mixture. The formation of particles should produce a marked change in the scattering of light. (If turbidity measurements are not sensitive enough to detect the initial formation of small primary particles, more powerful light scattering equipment may have to be purchased and utilized.) The molecular weight and conversion of the latex and serum will be measured from samples taken with initial styrene concentrations just below and just above that needed for particle formation. GPC and GC analysis will be used for measuring the molecular weight and conversion, respectively. HDC analysis of the latex will provide particle size (number) data. Using this information plus the overall conversion of the individual monomers, the critical chain length at which particle nucleation occurs in the aqueous phase can be estimated. This analysis may be repeated at different values of DN (pH). NMR analysis of the serum (and latex) may also provide information for determining j_{cr} .

(6) Oligomer composition - If r values can be obtained, estimations of the oligomer composition can be made using the copolymer composition equation. An alternative approach is to use NMR analysis.

Comparison of NMR spectra of acid and styrene homopolymers to acid-styrene copolymer spectra may provide enough information to back out the oligomer composition and possibly the monomer sequence distribution. NMR techniques used for other copolymer systems such as MMA-MAA may be applicable.

V. NOMENCLATURE

C	-	moles of total acid monomer in the system
f	-	initiator efficiency
f_i	-	instantaneous fraction of monomer in the feed
F_i	-	instantaneous fraction of monomer in the copolymer
$[I]$	-	initiator concentration
K	-	dissociation constant
k_c	-	rate constant for radical capture
k_{cs}	-	rate constant for radical capture by seed latex
k_d	-	initiator decomposition constant
k_{des}	-	radical desorption constant
k_i	-	rate constant for initiation
k_{NS}	-	rate coefficient for capture of primary particles by latex particles
k_p	-	rate constant for propagation
k_t	-	overall rate constant for termination
k_{tc}	-	rate constant for termination by coupling
k_{td}	-	rate constant for termination by disproportionation
k_{tw}	-	rate constant for termination in the water phase
L	-	distance traveled during time needed for polymerization to the critical chain length
$[M_i]$	-	concentration of monomer i (moles/L)
$[M_t]$	-	total monomer concentration at time t (moles/L)
N	-	number of particles (particles/cm ³ water)
N_A	-	Avogadro's number
n_i	-	average number of radicals i /particle
r_i	-	reactivity ratio

$[R^*]$	-	concentration of free radicals (mole/L)
R_i	-	rate of initiation (moles/L · time)
R_j	-	number of oligomer radicals with j monomer units
R_0	-	total concentration of radicals
R_p	-	rate of polymerization (moles/L*time)
$[S_e]$	-	concentration of surfactant
t	-	time
V	-	volume (L)
V_p	-	particle volume

GREEK

α	-	fraction of dissociated acid
α_o	-	distribution coefficient of monomer <u>a</u> between the particle and water phases
β	-	degree of ionization of the radicals
β_o	-	distribution coefficient of monomer <u>b</u> between the particle and water phases
ϕ	-	cross termination coefficient
ρ	-	polymer density
ρ_a	-	rate of radical adsorption by particles
ρ_c	-	rate of coagulation of primary particles
ρ_i	-	rate of generation of radicals
τ_p	-	average life of free radical in polymer particles
μ	-	rate of volume increase of particles in Interval I

SUBSCRIPTS

a	-	monomer a (acid)
aq	-	aqueous
b	-	monomer b
cr	-	critical chain length
o	-	initial time of reaction ($t=0$)
p	-	particle
s	-	seed
t	-	termination
w	-	aqueous (water) phase

VI. REFERENCES

1. G. Odian, Principles of Polymerization, John Wiley and Sons, NY (1981).
2. V.F. Gromov, N.I. Galperina, T.O. Osmanov, P.M. Khomikovskii, and A.D. Abkin, European Polym. Journal, **16**, 529, (1980).
3. N.I. Galperina, T.A. Gugunaua, V.F. Gromov, P.M. Khomokovskii, and A.D. Abkin, Vysokomol. Soyed., **A17**, 1455, (1975).
4. A. Katchalsky and G. Blauer, Faraday Soc. Trans., **47**, 1360, (1951).
5. S.H. Pinner, J. Poly. Sci., **9**, 282, (1952).
6. G. Blauer, J. Poly. Sci., **11**, 189 (1953).
7. E.P. Bonsall, L. Valentina, H.W. Melville, J. Poly. Sci., **7**, 39, (1951).
8. I.M. Kolthoff and I.K. Miller, J. Amer. Chem. Soc., **73**, 3055, (1951).
9. H.J. Van den Hul and J.W. Vanderhoff, BR. Polym. J., **2**, 121, (1970).
10. W.D. Harkins, J. Poly. Sci., **5**, 217 (1950); J. Am. Chem. Soc., **69**, 1428 (1947).
11. W.V. Smith and R.H. Ewart, J. Chem. Phys., **16**, 592 (1948).
12. W.H. Stockmayer, J. Poly. Sci., **24**, 314 (1952).
13. J.L. O'Toole, J. Appl. Poly. Sci., **9**, 1291 (1965).
14. J. Ugelstad and P.C. Mork, Br. Polym. J., **2**, 31 (1970).
15. R.M. Fitch, in "Emulsion Polymers and Emulsion Polymerization", D.R. Basset and A.E. Hamielec, eds, ACS Sympos., Washington, D.C., **165**, 1 (1981).
16. W.J. Priest, J. Phys. Chem., **56**, 1077 (1952).
17. R.M. Fitch and C.H. Tsai, Polymer Colloids, Plenum Press, NY, **73**, (1970).
18. F.K. Hansen and J. Ugelstad, J. Poly. Sci., Poly. Che. Ed., **16**, 1953, (1978).
19. Z. Song, PhD Proposal, School of ChE, Ga. Inst. of Tech, unpublished, (1986).

20. H.W. Melville, B. Noble, and W.F. Watson, J. Poly. Sci., 2, 229 (1947).
21. C. Walling, J. Am. Chem. Soc., 71, 1930 (1949).
22. S.W. Bensen and A.M. North, J Am. Chem. Soc., 81, 1339 (1959).
23. A.M. North and G.A. Reed, Trans. Faraday Soc., 57, 859 (1961).
24. P.E.M. Allen and C.R. Patrick, Makromol. Chem., 47, 154 (1961).
25. J.N. Atherton, A.M. North, Trans, Faraday Soc., 58, 2049 (1962).
26. H. Schuller, "Copolymerization in Emulsion", in Polymer Reaction Engineering, K.-H. Riechert and W. Geiseler, Eds., Huthig and Wepf, Germany, (1986).
27. M. Nomura, K. Yamamoto, I. Horie, and K. Fujita, J. Appl. Poly. Sci., 27, 2483 (1982).
28. R.N. Mead, PhD Thesis in progress, Georgia Inst. of Tech, (1987).
29. K. Sakota and T. Okaya, J. Appl. Poly. Sci., 20, 3265 (1976).
30. Matsumoto and Shimada, Kobunshi Kagaku, 22, 172, (1965).
31. T. Alfrey, Jr. and G. Goldfinger, J. Chem. Phys., 12, 322 (1944).
32. H. Ito and S. Suzusuki, Kogyo Kagaku Zasshi, 58, 627 (1955).
33. M.K. Mishra and S.N. Bhadani, Makromol. Chem., 184, 955, (1983).
34. M. Mandel, Eur. Poly. J., 6, 807, (1970).
35. J.C. Leyte and M. Mandel, J. Poly Sci.:Pt. A, 2, 1879, (1964).
36. H.P. Gregor and M. Frederick, J. Poly. Sc., 23, 451, (1957).
37. S. Muroi, J. Poly. Sci., 10, 713, (1966).
38. B.R. Vijayendran, J. Appli. Poly. Sci., 23, 893, (1979).
39. K. Sakota and T. Okaya, J. Appl. Poly. Sci., 21, 1035, (1977).
40. S. Egusa and K. Makinuchi, J. Poly. Sci., 20, 863, (1982).
41. W. Ceska, J. Appl. Poly. Sci., 18, 427, (1974).
42. W. Ceska, J. Appl. Poly. Sci., 18, 2493, (1974).
43. R.G. Fordyce and G.E. Ham, J. Am. Chem. Soc., 69, 695, (1947).

44. S.P. Gasper and J.S. Tan, in Water Soluble Synthetic Polymers: Properties and Behavior by P. Molyneux, Vol.I, CRC Press (1983).
45. F.L. Martin, and A.E. Hamielec, ACS Symposium Series.104,43, (1978).
46. K. Sakota and T. Okaya, J. Appl. Poly. Sci., 20, 3255, (1976).
47. Ibid. p. 2583.
48. F.V. Loncar, M.S. El-Aasser, and J.W. Vanderhoff, "Emulsion Polymerization", American Chemical Soc. Meeting, New York, April (1986).
49. S. Nishida, PhD Thesis, Lehigh Univ., (1980).
50. G. Blauer, Faraday Soc. Trans., 56, 606, (1960).
51. K.M. Jones, D Bhattacharya, J.L. Brash and A.E. Hamielec, Polymer,27, 602, (1986).
52. D. Bhattacharya and A.E. Hamielec, Polymer, 27, 611, (1986).
53. L.H. Garcia-Rubio, M.G. Lord, J.F. MacGregor and A.E. Hamielec, Polymer,26, (1985).
54. F.L. Martin and A.E. Hamielec, J. Appl. Polym. Sci., 27, 489, (1982).

BATCH EMULSION COPOLYMERIZATION WITH CARBOXYLIC ACIDS

PROGRESS REPORT 1

PERIOD: 7/87 - 11/87

GLENN L. SHOAF

DIRECTED BY DR. G. W. POEHLEIN

GEORGIA INSTITUTE OF TECHNOLOGY

ATLANTA, GEORGIA 30332

CORPORATE SPONSOR: DOW CHEMICAL

MIDLAND, MICHIGAN

Introduction

Aspects of work currently being conducted in the area of batch emulsion copolymerization with carboxylic acids are described in this report. Initial studies have involved separate polymerizations of methacrylic acid (MAA) and acrylic acid (AA) in water solutions under various reaction conditions. Proposed kinetic models for the reaction of these acids are discussed. Monomer partitioning data for acid (AA or MAA)/styrene systems is presented. Thermodynamic equations for monomer partitioning between the aqueous, particle, and droplet phases are also presented along with values of different interaction parameters which were fitted to experimental data for these two comonomer systems. A proposed emulsion copolymerization kinetic model which includes aqueous-phase polymerization is briefly discussed. Also included are results of initial copolymerization runs in the presence of surfactant above its critical micelle concentration. Finally, future work to be performed on this project is discussed.

Solution Polymerization Studies

Solution polymerizations of both MAA and AA were run under each of the conditions listed in Table 1. We assumed that any interaction between the parameters was negligible.

Table 1 - Conditions Used for Solution Polymerizations of Both
MAA and AA

<u>Concentration Acid (Wt.%)</u>	<u>Degree of Neutralization</u>	<u>Temperature (°C)</u>
2.0	0	85
4.0	0	85
7.0	0	85
10.0	0	85
7.0	0.25	85
7.0	0.50	85
7.0	0.75	85
7.0	1.00	85
7.0	0	70
7.0	0	80
7.0	0	90
7.0	0	96 - 98

Conversion-time curves for the natural pH (DN=0) reactions of MAA and AA at 85°C over a range of concentration from 2.0 to 10.0 wt. % are shown in Figures 1 and 2. A reaction model Eq. (1) which has been shown to apply to many simple free-radical solution polymerizations was used for preliminary examination of the experimental data.

$$R_p = -dM/dt = (k_p/k_t^{1/2}) (f k_d [I])^{1/2} [M] \quad (\text{mole/L s}) \quad (1)$$

where, k_p = propagation constant (L/mole s)
 k_t = termination constant (L/mole s)
 k_d = initiator decomposition constant (1/s)
 f = initiator efficiency factor (assumed = 1.0)
 $[I]$ = concentration of initiator (mole/L)
 $[M]$ = concentration of monomer (mole/L)
 t = time (s)

CONV. VS. TIME FOR METHACRYLIC ACID

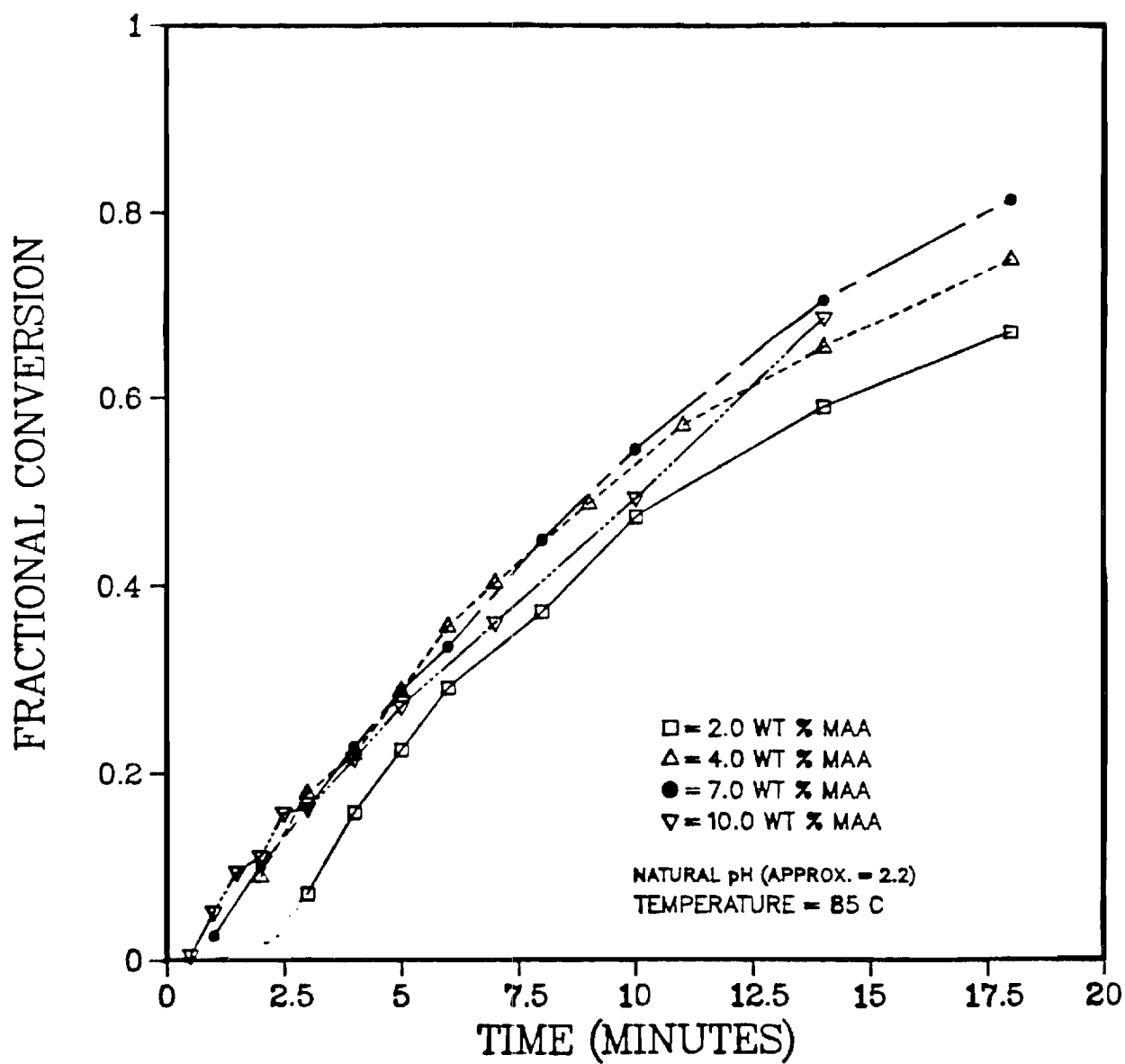


Figure 1 - MAA Conversion-time Curves at Various Monomer Concentrations

CONVERSION VS. TIME FOR ACRYLIC ACID

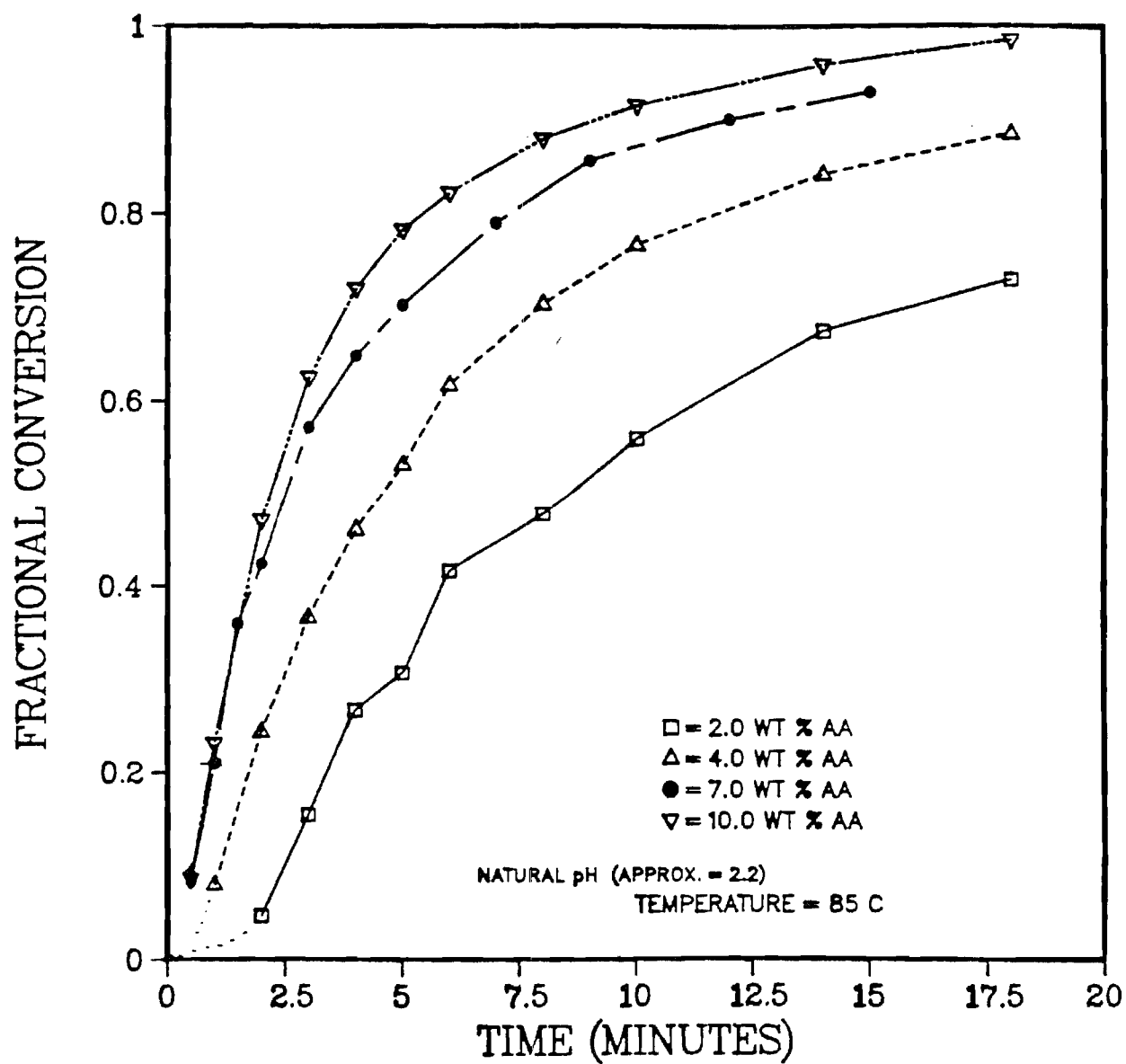


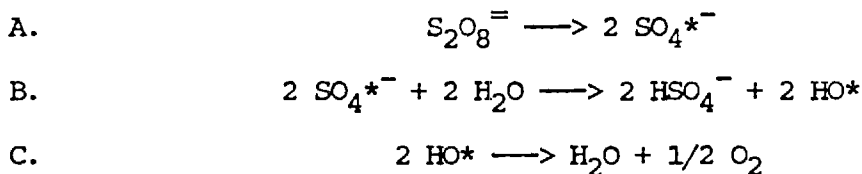
Figure 2 - AA Conversion-time Curves at Various Monomer Concentrations

Integration of Eq. (1), assuming that all parameters except $[M]$ are time invariant, gives Eq. (2),

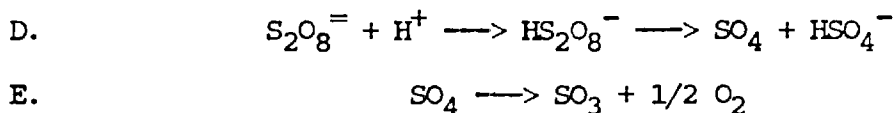
$$\ln [M]_0/[M] = (k_p/k_t^{1/2}) (f k_d [I])^{1/2} t = K t \quad (2)$$

Reaction samples were collected over time, and monomer conversions were measured gravimetrically. $[I]$ was known a priori. A value of k_d of 6.89×10^{-5} (1/s) for potassium persulfate was obtained from the literature [1]. Several workers have shown that k_d increases at low pH [2,3]. The increase, however, is attributed mainly to an increase in the catalyzed reaction. This reaction does not contribute to the formation of free radicals as shown below:

Uncatalyzed Reaction



Catalyzed Reaction



Data for the decomposition of potassium persulfate at 50°C suggests that the uncatalyzed reaction rate may tend to increase slightly at low pH [2]. These workers did not measure reaction rates at low pH with higher temperatures. However, the pH effect ^{on the uncatalyzed reaction} again is expected to be relatively small based on the reactions listed above.

Plots of $\ln[M]_0/[M]$ versus time should be linear with a slope of K based on the relationship given by Eq. (2). $k_p/k_t^{1/2}$ can then be obtained from the slope. Gromov et. al. [4] report values of k_t for MAA (0.12×10^8 L/mole s) and AA (1.8×10^8 L/mole s) as obtained from experiments utilizing the method of alternating illumination. If these termination rate constants are utilized, propagation constants can be calculated directly from $k_p/k_t^{1/2}$ ratios. Values of $k_p/k_t^{1/2}$ and k_p (L/mole s) obtained from the experimental data as well as those predicted from Gromov's data are listed in Table 2 for the range of monomer concentrations investigated. Gromov [4] assumed that the reaction rate given by Eq. (1) applied to both AA and MAA solution polymerizations. The value of k_p should then be independent of monomer concentration as depicted in Table 2. He does not specifically state the actual monomer concentrations utilized in his experiments. However, similar work which he performed with Galperina [5] involved reactions of AA at concentrations of 3.0 to 4.0 Wt. %. The values based on Gromov's data as listed in Table 2 were obtained by fitting an Arrhenius expression to ^{the} ~~Gromov's~~ data (which were given for temperature ranges of 0 to 60°C) and extrapolating to 85°C, the temperature at which experimental data listed in Table 2 were obtained. These experiments as well as Gromov's were performed at natural pH (approximately 2.2).

Table 2 - $k_p/k_t^{1/2}$ and k_p Values for MAA and AA

<u>AA</u>					
Wt. %	$k_p/k_t^{1/2}$		$k_p \left(\frac{L}{mole.s} \right)$		k_p (Gromov)
	Replicate 1	Replicate 2	Replicate 1	Replicate 2	
2.0	6.05	5.68	81160	76200	76969
4.0	11.94	10.85	160160	145560	"
7.0	18.08	15.31	242560	205370	"
10.0	20.61	20.57	276520	276050	"
<u>MAA</u>					
2.0	4.37		15148		15919
4.0	5.24		18157		"
7.0	4.89		16954		"
10.0	4.34		15045		"

Values of k_p are plotted as a function of initial monomer weight percent for MAA in Figure 3. The data for MAA agree fairly well (within experimental error) with the k_p values predicted from Gromov's data. The $\ln[M]_0/[M]$ versus time data are shown in Figures 4a-d. The data fall on relatively straight lines as predicted by the assumed first order kinetic model given by (1).

k_p data for AA is plotted in Figure 5. The k_p values increase substantially as the initial monomer weight percent increases. They also differ greatly from the values predicted from Gromov's data for initial monomer concentrations greater than 2.0 wt. %. Figures 6a-d reveal that the $\ln[M]_0/[M]$ versus time data deviates from straight line behavior at the higher conversions. The simple first order kinetic model, therefore, does not apply to the AA solution polymerization.

MAA PROPAGATION CONSTANT - 85 C

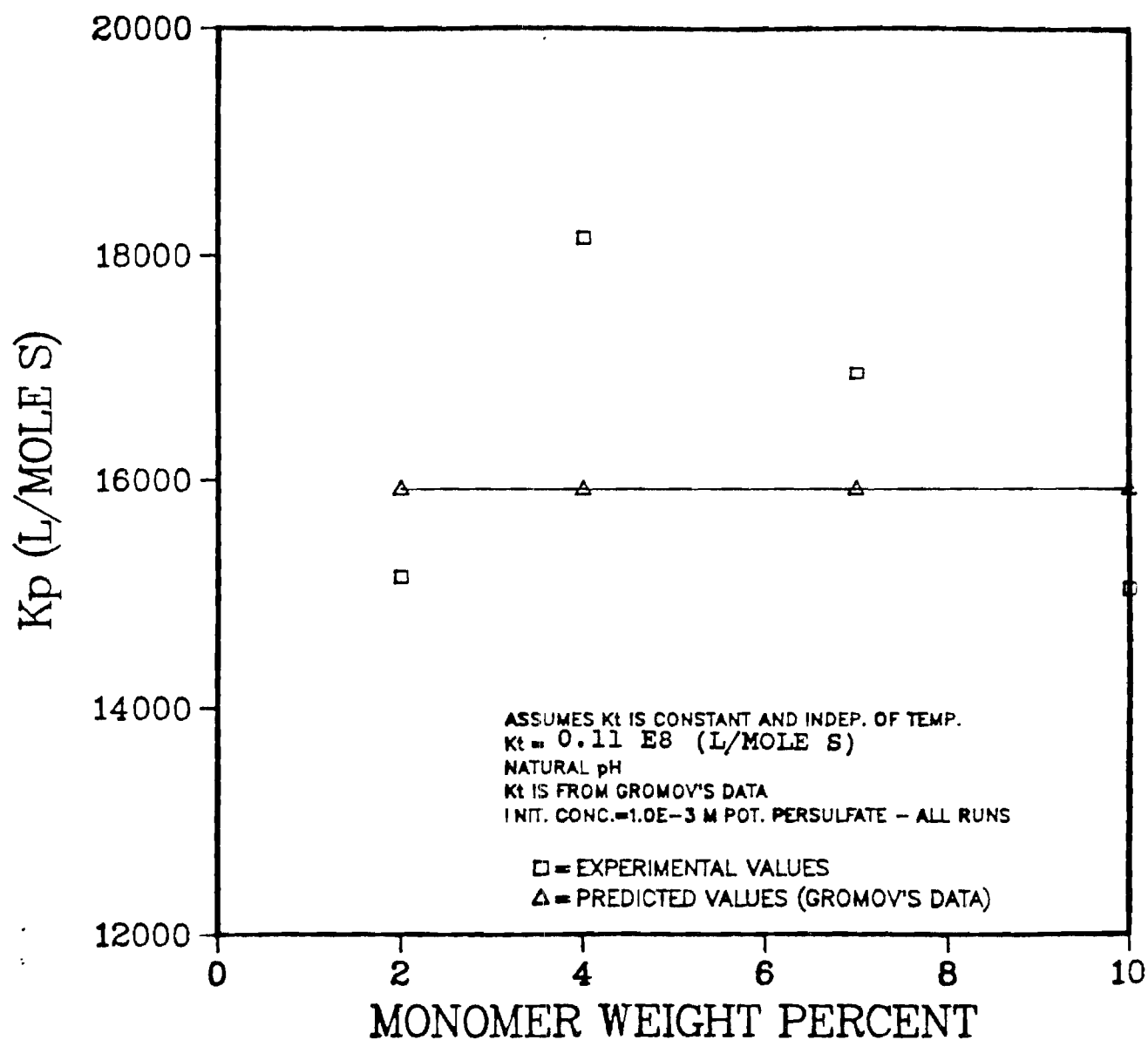
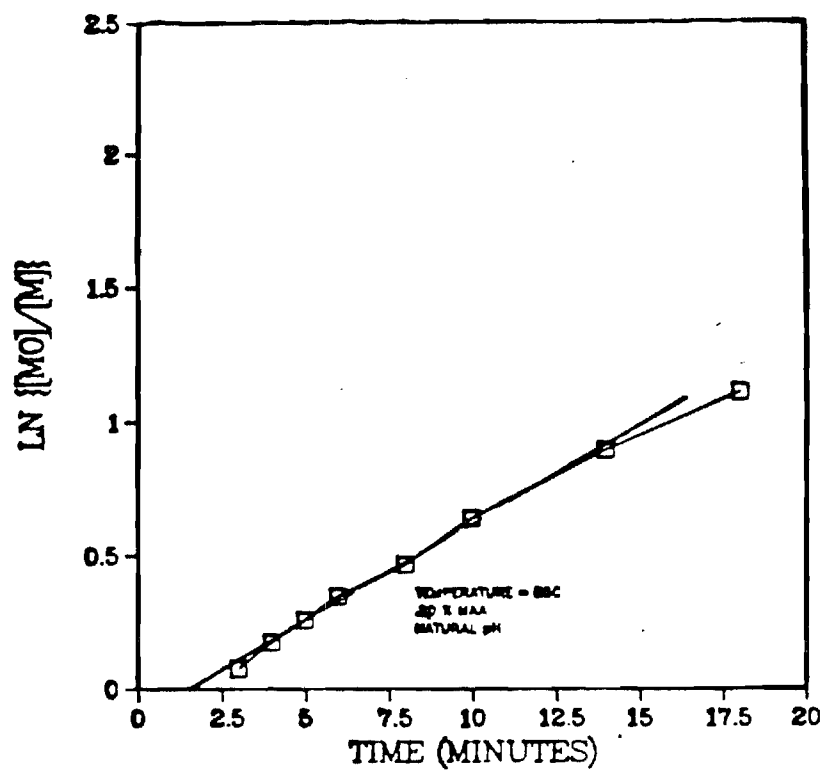


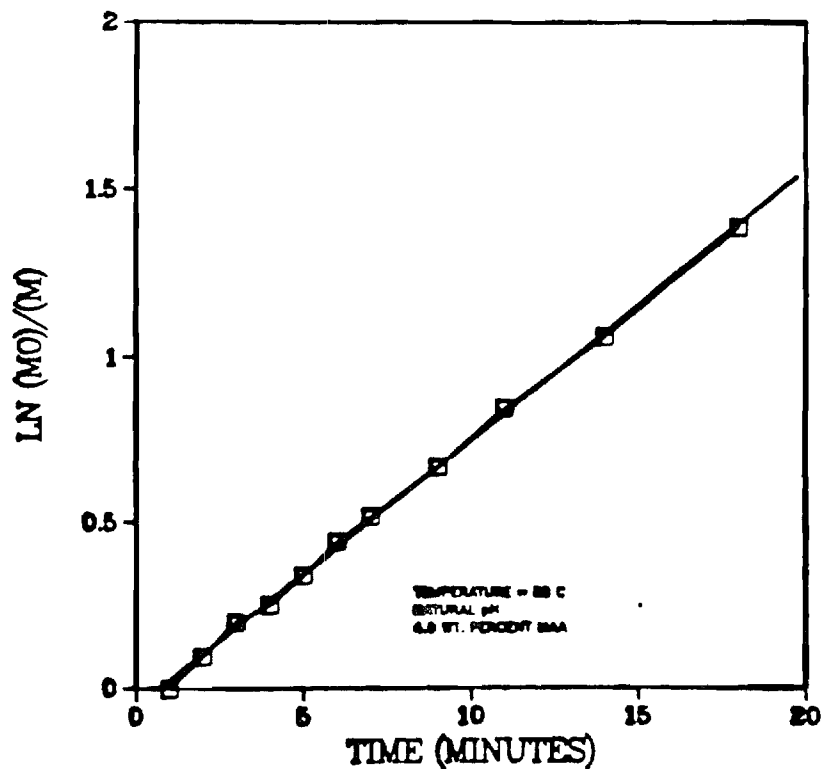
Figure 3 - MAA Propagation Constant as a Function of Initial Monomer Concentration

HMAA3 - R



4a

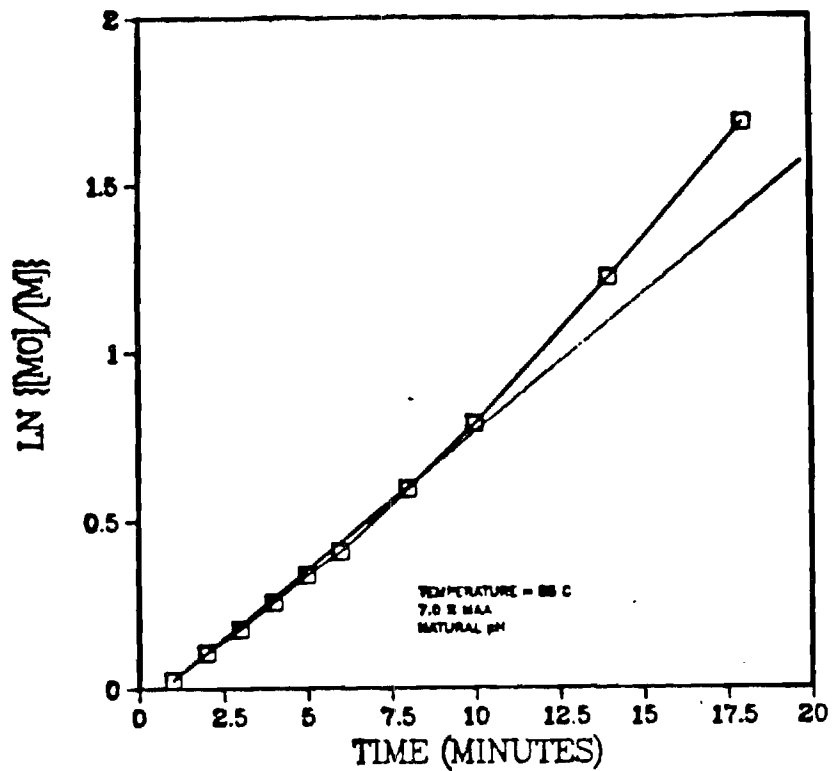
HMAA-2



4b

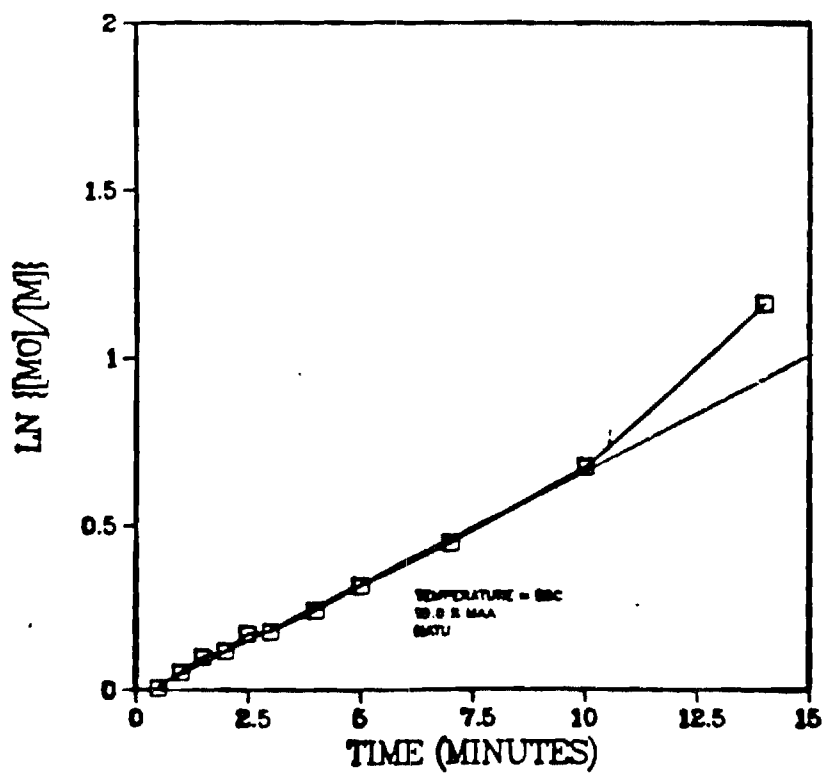
Figure 4 - $\ln [MO]/[M]$ versus Time at Various MAA Concentrations

HMAA-4



4c

HMAA-5



4d

Figure 4 - $\ln [M]_o/[M]$ versus Time at Various
(continued) MAA Concentrations

AA PROPAGATION CONSTANT - 85 C

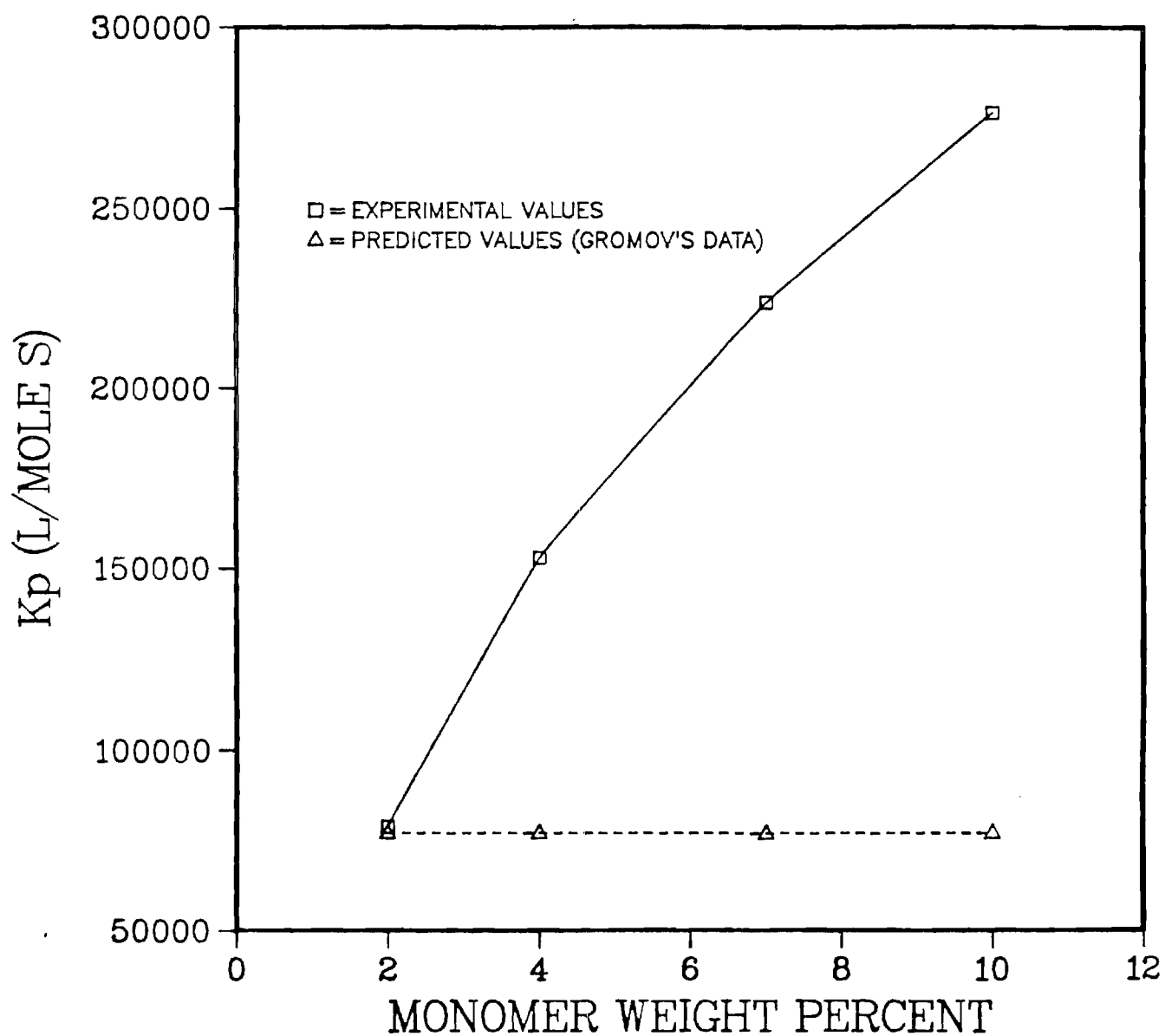
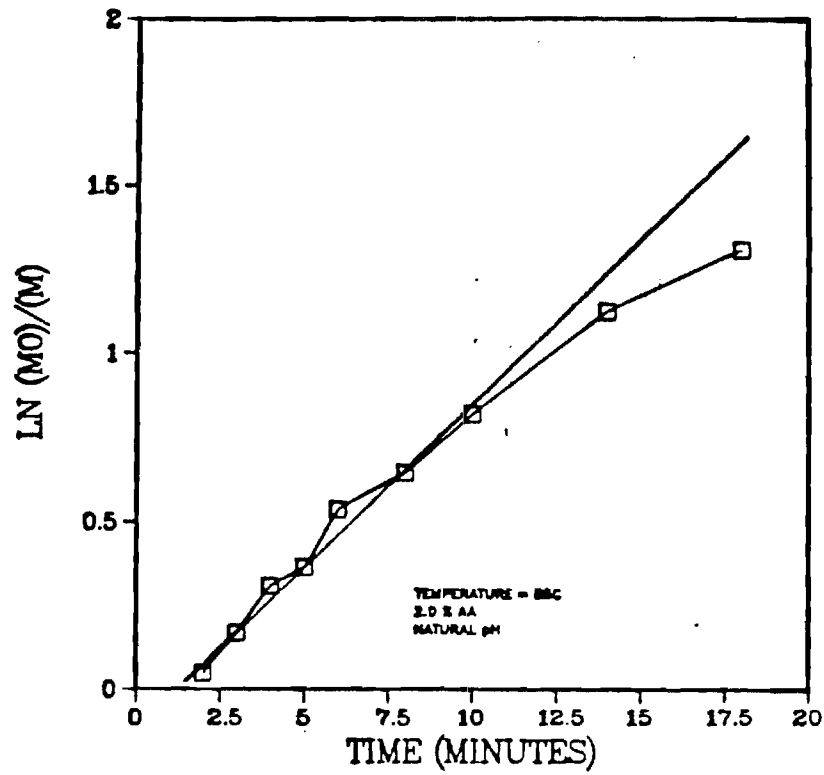


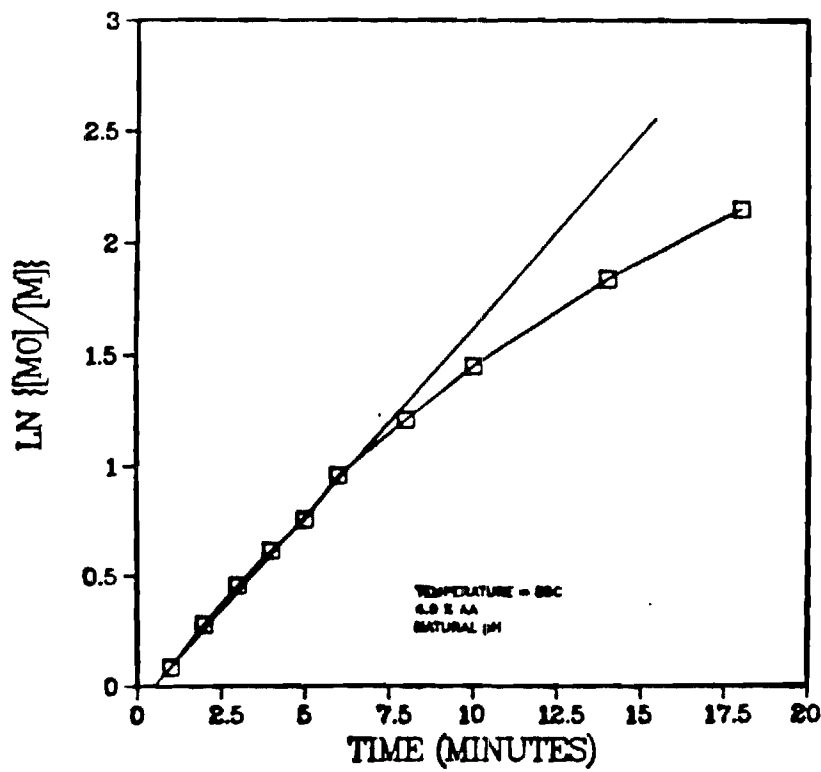
Figure 5 - AA Propagation Constant as a Function of Initial Monomer Concentration

HAA-9



6a

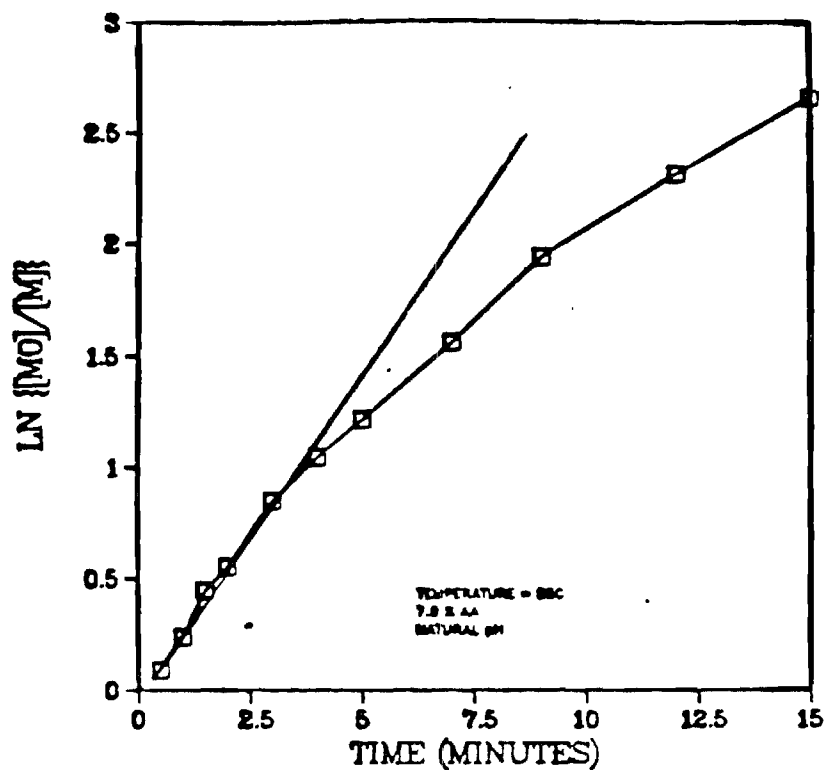
HAA-10R



6b

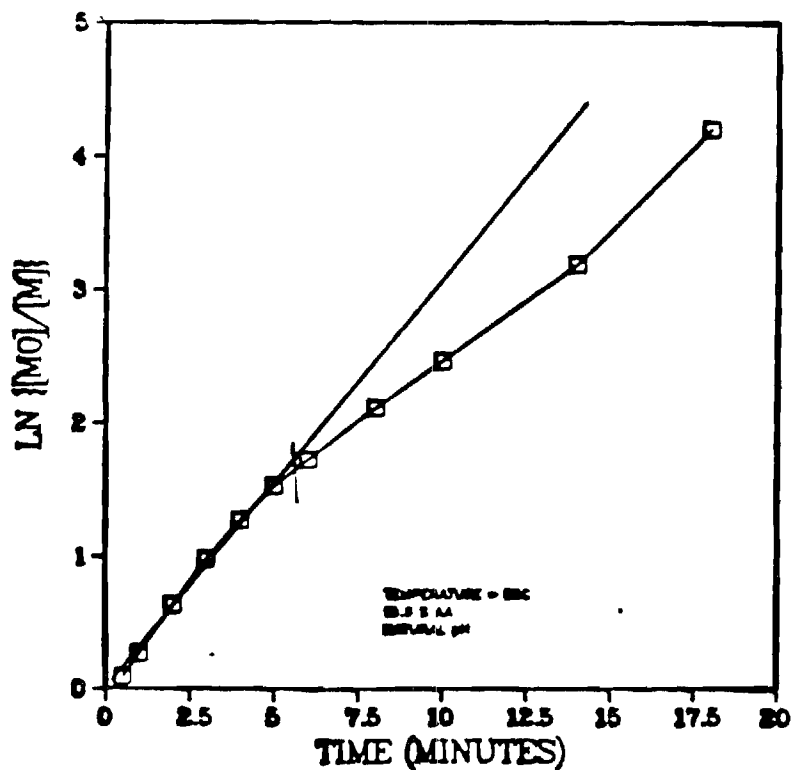
Figure 6 - $\ln [M]_0/[M]$ versus Time at Various AA Concentrations

HAA-8R2



6c

HAA - 11R



6d

Figure 6 - $\ln \frac{[MO]}{[M]}$ versus Time at Various
(continued) AA Concentrations

Further investigation leading to a more complex proposed kinetic model has been conducted and will be discussed later.

Propagation constants were also obtained as a function of temperature. Application of an Arrhenius relationship, Eq. (3) suggests that a plot of $\log k_p$ versus $1/T$ should yield a straight line with a slope of E_p (activation energy) and intercept of A_p (pre-exponential factor).

$$k_p = A_p \exp(-E_p/RT) \quad (3)$$

where, T = temperature (K)
 R = gas constant

Plots of k_p (log scale) versus $1/T$ for MAA and AA, shown in Figures 7 and 8, respectively, form relatively straight lines. Values of A_p and E_p , calculated as described above, are listed in Table 4 along with values reported by Gromov et al. [2].

Table 4 - Arrhenius Constants for MAA and AA

	A_p exp (L/mole s)	A_p Gromov (L/mole s)	E_p exp (kcal/mole)	E_p Gromov (kcal/mole)
MAA	4.76×10^{12}	0.67×10^7	13.86	4.3
AA	2.73×10^{14}	0.60×10^7	14.91	3.1

The experimental values are much greater than those reported by Gromov [4]. Values reported for similar monomers are also of the order of those reported by Gromov [4]. One explanation for the large

K_p vs. RECIPROCAL TEMPERATURE (MAA)

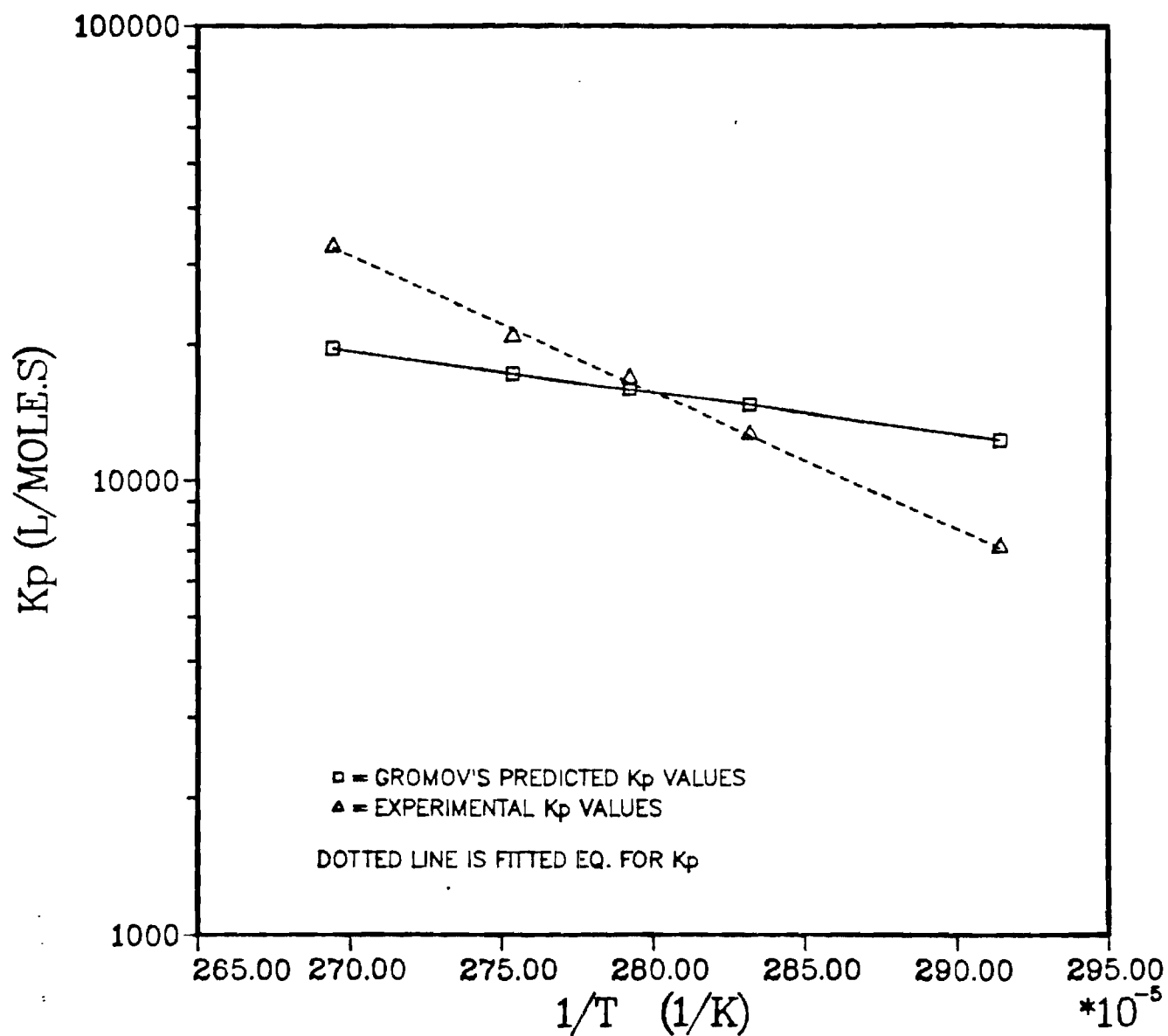


Figure 7 - Dependence of k_p on Temperature for MAA

K_p vs. RECIPROCAL TEMPERATURE (AA)

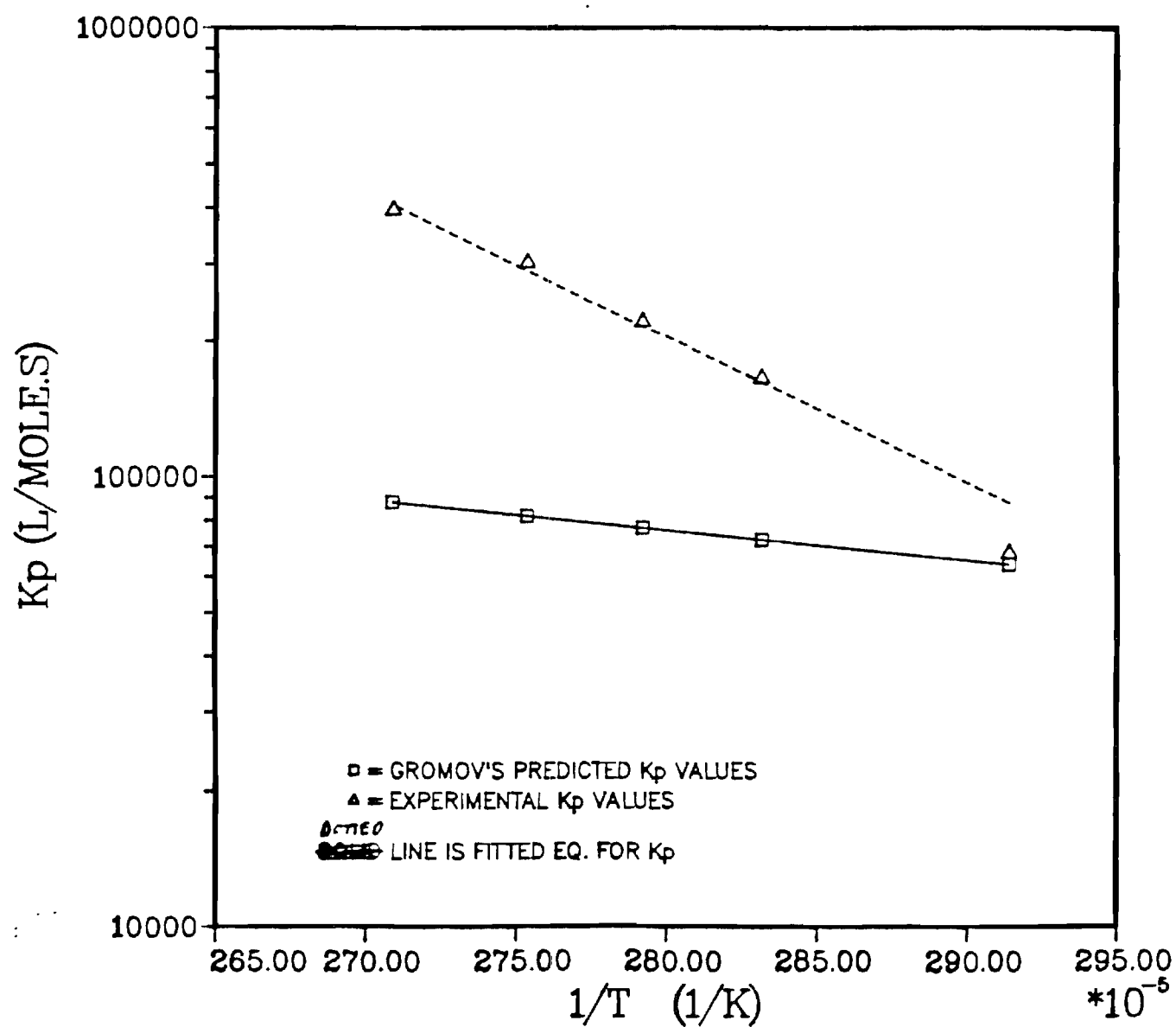


Figure 8 - Dependence of k_p on Temperature for AA

discrepancy may be due to a "false compensation" effect. If reaction rates are measured over fairly small ranges of temperature, (30°C as used here is considered very small) use of the data in an Arrhenius expression may produce considerable error in both E_p and A_p in the same direction. A positive error in E_p results in a positive error in A_p which thus results in false compensation. k_p data over a much larger temperature range would be necessary for determining the significance of this effect.

The propagation constants used to obtain the Arrhenius constants for both MAA and AA were calculated based on the first order rate expression given by Eq. (1). Conversion data suggest that this model is inappropriate for AA. Therefore, the k_p values for AA used to calculate the Arrhenius constants may also be inappropriate, thus contributing to the discrepancy discussed above.

Solution polymerizations were run at various degrees of neutralization (DN). Initial rates for MAA and AA are shown as a function of DN in Figures 9 and 10, respectively. Initial rates decreased significantly for each monomer as the DN increased from 0 to 1.0. This behavior is explained by the lower reactivity of the anionic form of the monomer due to electrostatic repulsion between the anions. An additional factor which may contribute to the decrease in rate at increased values of DN may also be related to a less ordered alignment of the monomers due to decreased hydrogen-bonding when the monomer is ionized, especially in the case of AA. Further discussion of this topic follows in the next section.

INITIAL RXN. RATES OF MAA AS f (DN)

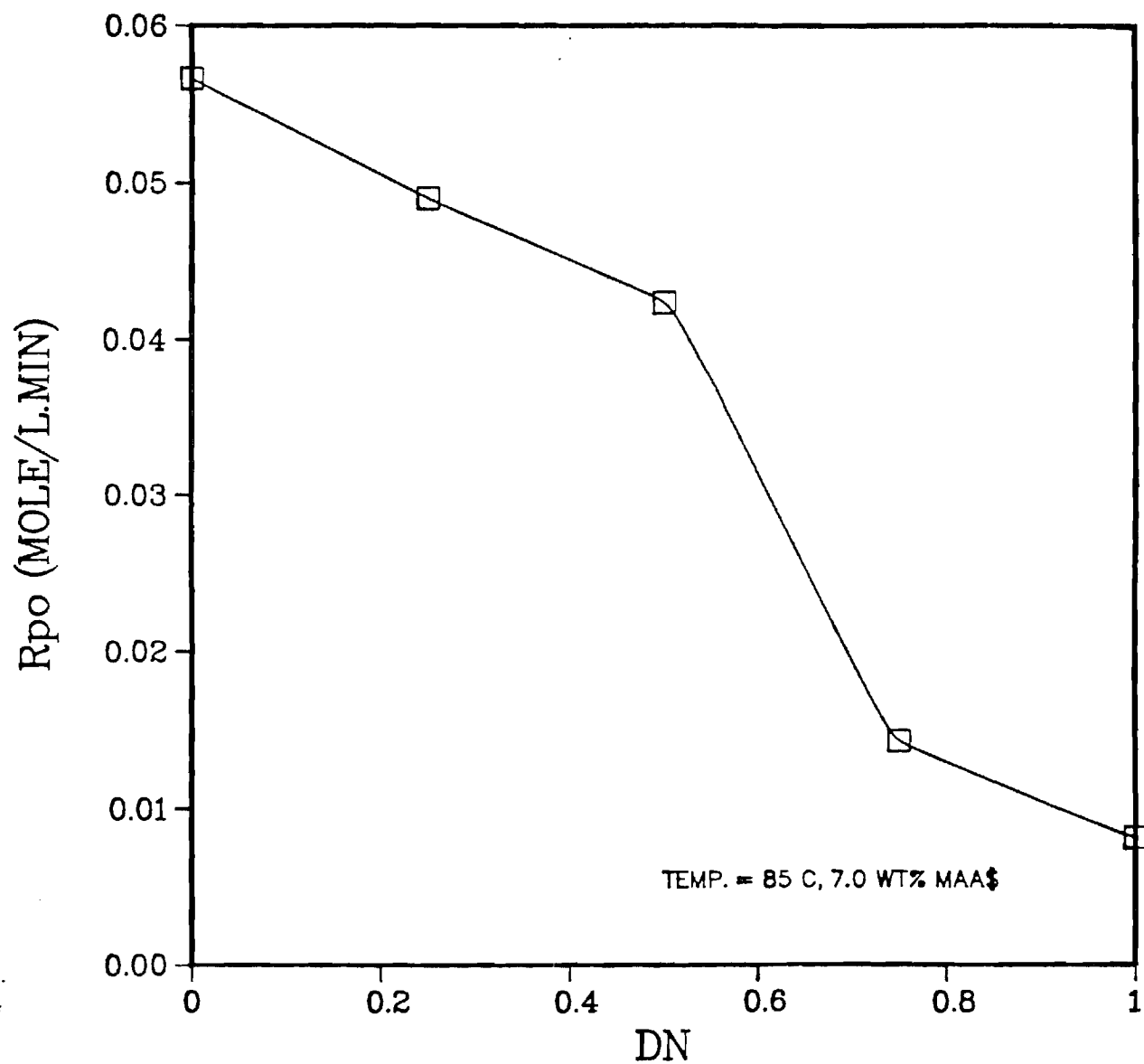


Figure 9 - Change of Initial Reaction Rates with DN for MAA

Rpo VS. DN - AA

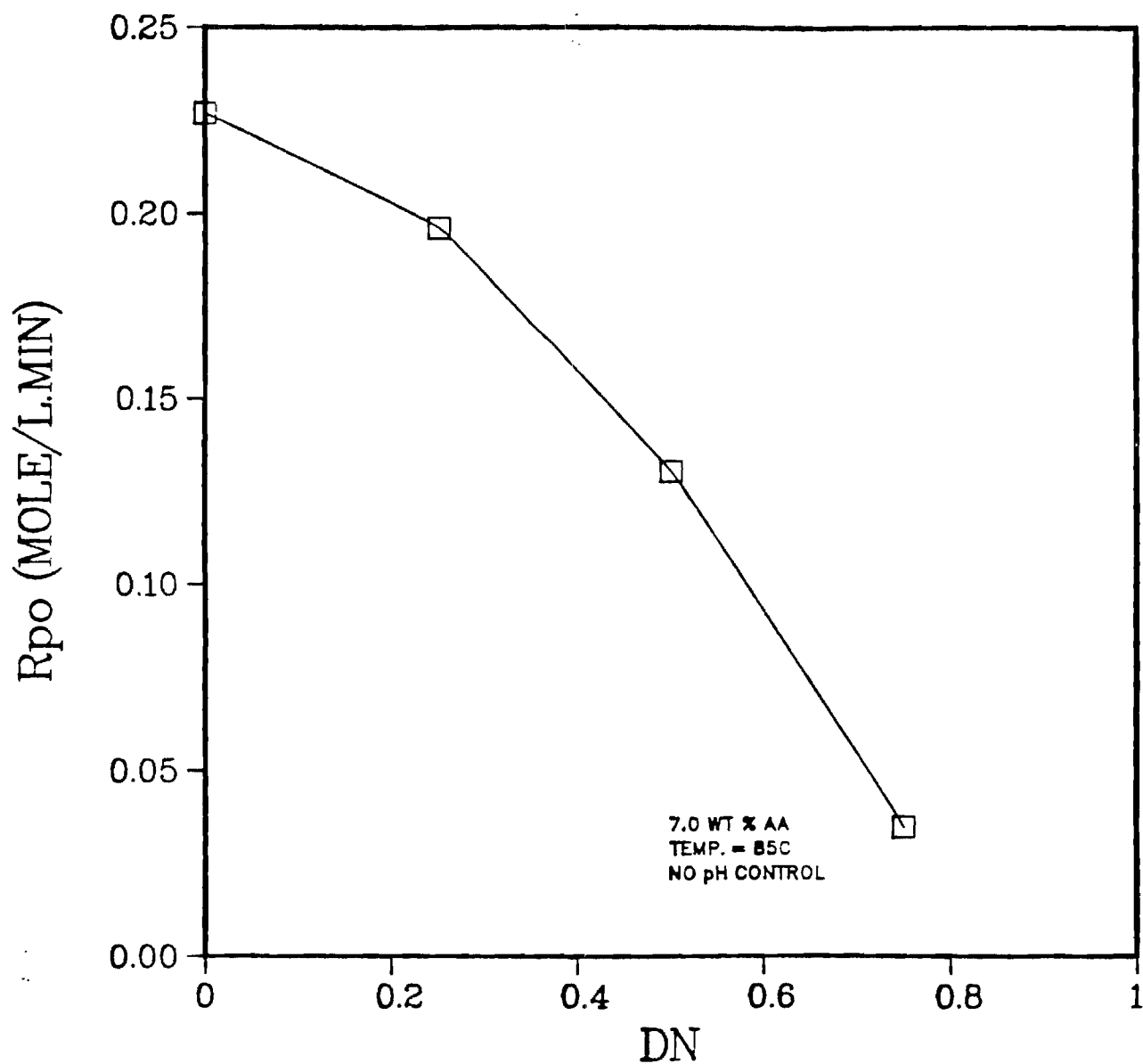
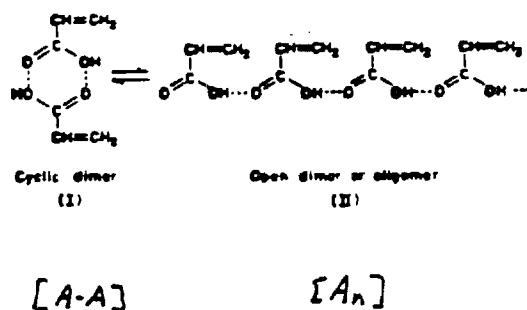


Figure 10 - Change of Initial Reaction Rates with DN for AA

Carboxylic acids are known to associate via hydrogen bonds to form cyclic dimers (Structure I) [6]. Other workers [7-9] have also shown that "open dimers" or "oligomers" may also form from these acid species (Structure II). Chapiro [10] presents viscosity curves for AA in various solvents (Figure 11). The initial increase in viscosity as the concentration of AA is increased confirms the presence of "plurimolecular aggregates" or "linear oligomers". These oligomeric structures may tend to increase the "local" concentration of monomer thus enhancing the "local" rate of reaction.



If a carboxylic acid polymer is present, hydrogen bonding may also enhance the association of monomer and polymer as shown in Structure III. When a free radical initiates polymerization of a monomer unit aligned along a polymer chain as in Structure III, the reaction may zip along the chain due to the favorable alignment and high "local" concentration of other adjacent monomer units. A large degree of monomer association due to Structures II and III may significantly increase the rate of reaction relative to the reactions of a homogeneous mixture of single monomer units.

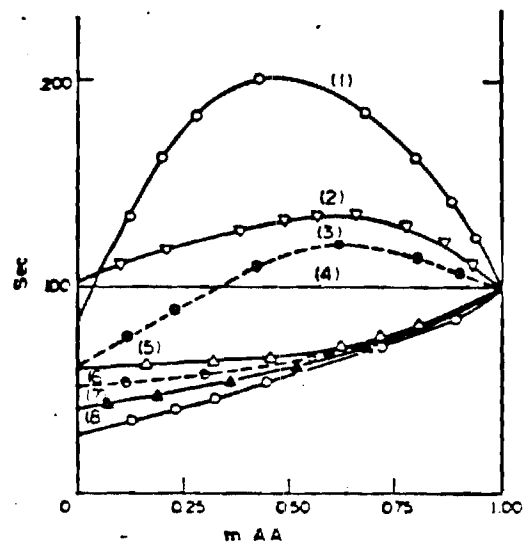
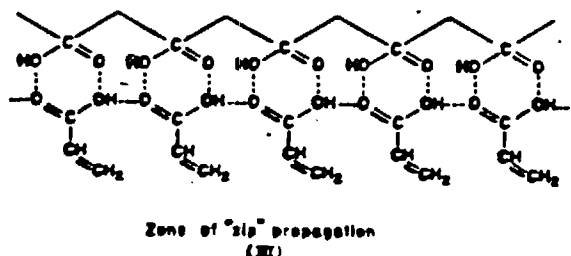


Fig. 8 Viscosity of acrylic acid dissolved in various solvents: flow times as a function of the mole fraction of monomer in: (1) water; (2) dioxane; (3) methanol; (4) acetic acid; (5) toluene; (6) carbon tetrachloride; (7) *n*-hexane; (8) chloroform.



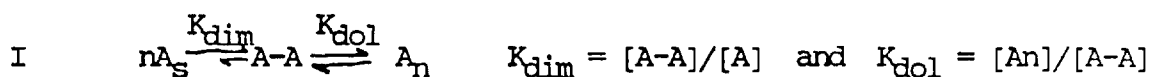
PA

(Structure III)

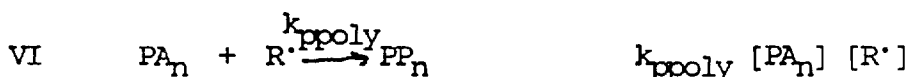
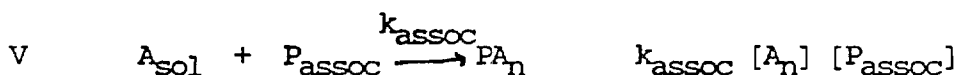
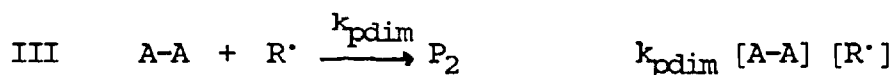
PP_n - polymer with reacted "oligomer" hydrogen-bonded to it

P₂ - reacted cyclic dimer

Proposed Reaction Mechanism



OR



A reaction model based on the proposed mechanism follows. The total rate of reaction is equivalent to the sum of the rates of AA monomer in the form of single molecules, dimers, hydrogen-bonded "oligomers", and monomer aligned along the backbone of AA polymer chains.

$$R_p \text{ tot} = -d[A]/dt = \cancel{R_{\text{ps}}} + R_p \text{ dim} + R_p \text{ olig} + R_p \text{ poly} \quad (4)$$

The concentration of single monomer molecules is very small such that R_{ps} is considered negligible. Substitution of the appropriate expressions into Eq. (4) then leads to Eq. (5).

$$R_p \text{ tot} = k_p \text{ dim } [A-A] [R^*] + k_p \text{ olig} [A_n] [R^*] + k_p \text{ poly } [PA_n] [R^*] \quad (5)$$

The concentration of AA monomer in solution not associated with polymer is defined by Eq. (6).

$$[A_{\text{sol}}] = \cancel{[A_s]} + [A-A]/2 + [A_n] = [A_{\text{tot}}] - [PA_n] \quad (6)$$

The concentration of "oligomeric" and dimeric AA monomer is given by Eqs. (7) and (8).

$$[A_n] = K_{\text{olig}} [A_{\text{sol}}] = K_{\text{olig}} ([A_{\text{tot}}] - [PA_n]) \quad (7)$$

$$[A-A] = 2(1-K_{\text{olig}}) [A_{\text{sol}}] = 2(1-K_{\text{olig}}) ([A_{\text{tot}}] - [PA_n]) \quad (8)$$

Substitution of Eqs. (7) and (8) in Eq. (5) gives Eq. (9).

$$\begin{aligned} -d[A_{\text{tot}}]/dt &= k_{p \text{ dim}} 2(1-K_{\text{olig}}) ([A_{\text{tot}}] - [PA_n]) [R^*] \\ &+ k_{p \text{ olig}} K_{\text{olig}} ([A_{\text{tot}}] - [PA_n]) [R^*] + k_p \text{ poly } [PA_n] [R^*] \end{aligned} \quad (9)$$

A balance around $[PA_n]$ leads to Eqs. (10).

$$d[PA_n]/dt = k_{\text{assoc}} ([A_{\text{tot}}] - [PA_n]) [P_{\text{assoc}}] - k_p \text{ poly } [PA_n] [R^*] \quad (10)$$

A similar balance around $[P_{\text{assoc}}]$ leads to Eq. (11)

$$d[P_{\text{assoc}}]/dt = k_p \text{ olig } [A_n] [R^*] - k_{\text{assoc}} [A_{\text{sol}}] [P_{\text{assoc}}] \quad (11)$$

Substitution of Eq. (8) into Eq. (11) leads to Eq. (11').

$$\begin{aligned} d[P_{\text{assoc}}]/dt = & k_{\text{polig}}K_{\text{olig}}([A_{\text{tot}}]-[PA_n]) \\ & - k_{\text{assoc}}([A_{\text{tot}}]-[PA_n])[P_{\text{assoc}}] \end{aligned} \quad (11')$$

Simultaneous solution of Eqs. (9), (10), and (11') then yields values for $[A_{\text{tot}}]$, $[PA_n]$, and $[P_{\text{assoc}}]$.

The linear polymer serves as a substrate or site along which the propagation reaction of AA may "zip" and thus functions much like a catalyst. However, since the monomer attached to this backbone becomes more sterically hindered after it reacts with adjacent units, it becomes less likely to break its hydrogen bonds and detach from the polymer. The polymer is in a sense "consumed" during the reaction since the sites for hydrogen-bonding are probably not freed for association with other monomer units after the initial hydrogen-bonded monomer has reacted. It, therefore, accelerates the reaction, but it should not be considered as a true catalyst.

Most carboxylic acid monomer molecules are associated in dimeric or oligomeric structures [6-9]. Therefore, the amount of polymer formed from reaction of single monomer molecules is likely to be very small. The reaction rate of dimeric monomers is small relative to monomer associated as oligomers or with monomer aligned along the polymer. Also, the polymer formed from dimers is cyclic in nature such that association with monomer via hydrogen-bonding similar to that of the linear polymer chains is very unlikely. Thus, most of the polymer formed during the AA solution polymerization most likely results from reaction of monomer associated as "oligomers" in solution and from reaction of monomer aligned along the backbone of polymer chains formed

from previous reaction of "oligomeric" monomer.

Determination of various constants in the model may be extremely difficult, and certainly additional experiments along with various simplifications of the model would be necessary to realistically quantify the reaction behavior. The model does, however, represent a more complete approach to the rather complex reaction of AA in solution than that of previous workers.

Some simulations using this model have been performed. Estimates of some of the rate constants were based on Chapiro's [10] work. Chapiro used initial rate and pseudo-stationary rate data to crudely estimate that $R_p \text{ olig} = 1/6 R_p \text{ poly}$ and $R_p \text{ dim} = 1/85 R_p \text{ poly}$. He assumed that $[PA_n]/[A_{tot}]$ was approximately 0.15 (based on measurements with bulk AA monomer [11]). Estimates of $k_p \text{ olig}$ and $k_p \text{ dim}$ for the simulations were made by writing appropriate expressions based on these estimated relationships between the rates.

$$k_{p \text{ olig}} = 0.15/(0.85*6) k_p \text{ poly}/K_{\text{olig}} \quad (12a)$$

$$k_{p \text{ dim}} = 0.15/(0.85*85) k_p \text{ poly}/(2(1-K_{\text{olig}})) \quad (12b)$$

A value for the free radical concentration was estimated by Eq. (13).

$$[R^{\cdot}] = (f k_d [I]/k_t)^{1/2} = 2.0 \times 10^{-8} \text{ (mole/L)} \quad (13)$$

Simulations were then run by initially adjusting k_{assoc} and $k_p \text{ poly}$. Adjustment of k_{assoc} had a strong influence on the value of $[PA_n]$ calculated, but it had little effect on the calculated value for $[A_{tot}]$ and thus conversion. Therefore, an arbitrary value of 100.0 was assumed for k_{assoc} and $k_p \text{ poly}$ was then adjusted to fit a set of

experimental data shown in Figure 11a. The value of k_p poly which gave a reasonable fit was 3,500,000 (L/mole s) which is much greater than the value obtained from calculation based on Eq. (1) or from Gromov's data. This would be expected since reaction of monomer aligned along a polymer backbone most likely "zips" along at relatively high rates.

Monomer Partitioning

The rate of reaction for an emulsion copolymerization with water-soluble monomer(s) depends on the rates of reaction in the particle and aqueous phases. The rates of reaction in each phase depends directly on the concentration of monomers in each reacting medium. Therefore, it is very important to understand how each monomer is partitioned between the aqueous phase, particles, and droplets.

Simple experiments involving mixtures of acid monomer, water, and styrene were conducted to observe the effects of monomer/water ratio and DN on the partition of the acid between the aqueous and organic phases. No polymer particles were present, and it was assumed that the concentration of styrene in the aqueous phase was negligible. Results of these experiments are revealed in Figures 12 and 13. Increasing the monomer/water ratio resulted in a significant increase in the fraction of MAA in the organic phase, but it produced almost no effect on the fraction of AA distributed between the two phases. The different partition behavior between the two monomers may be related to differences in hydrophobicity. MAA is more hydrophobic than AA. If the amount of acid is increased relative to the amount of water

EXPERIMENTAL AND SIMULATION OF AA POLY.

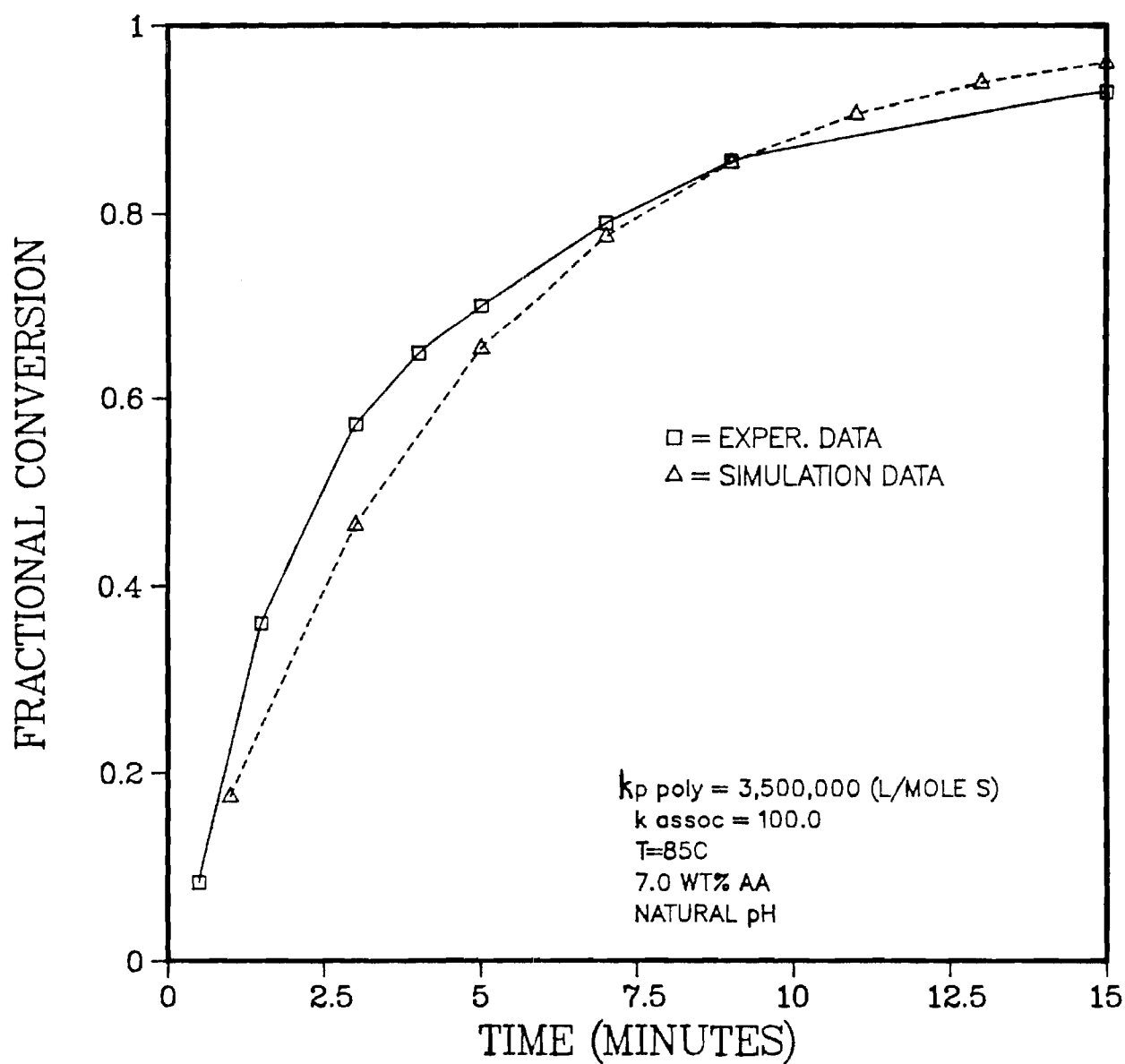


Figure 11a - Comparison of Experimental and Simulation Conversion Data for the Solution Polymerization of 7.0 WT% AA at 85C and natural pH.

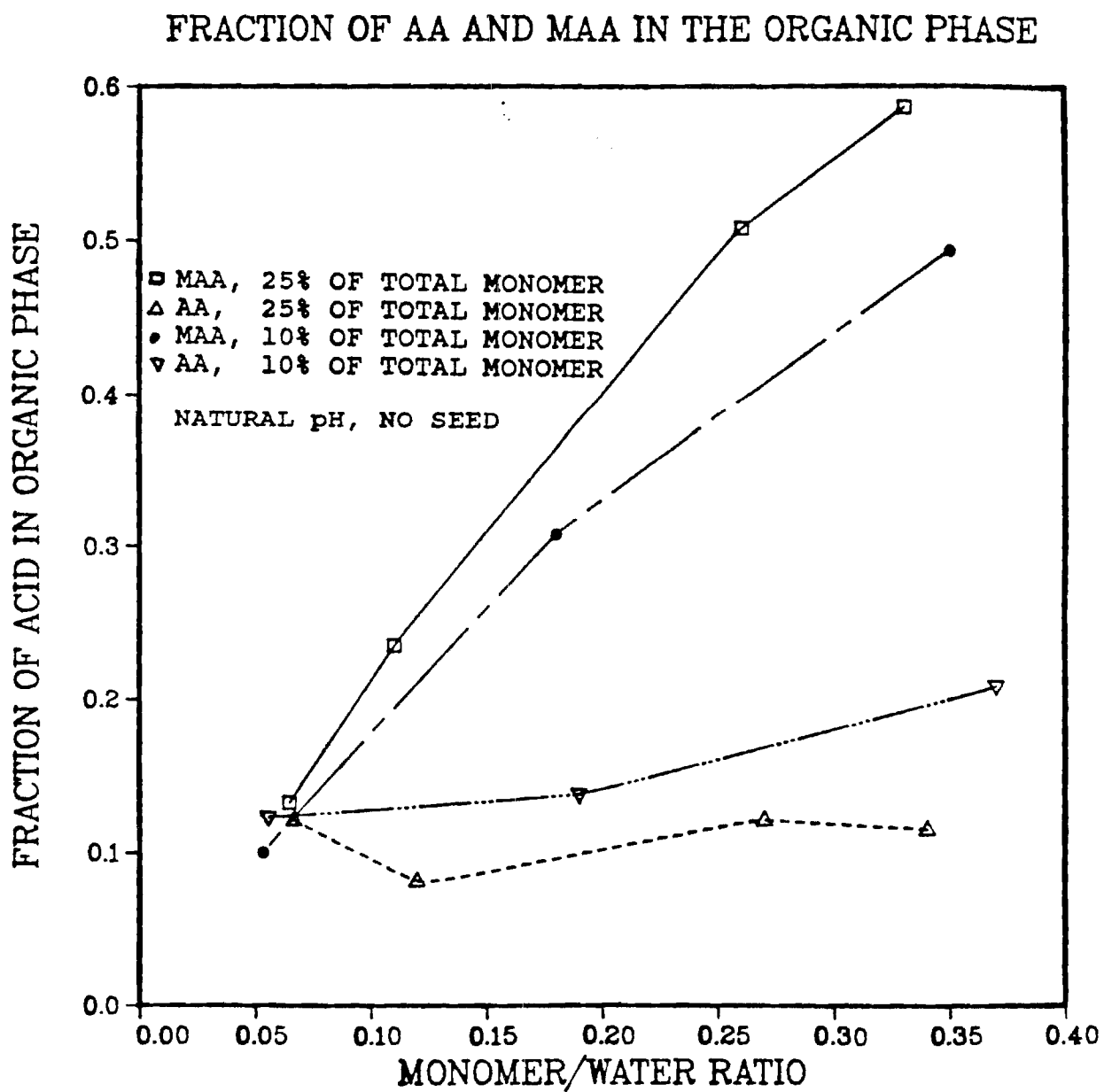


Figure 12 - Monomer Partition of AA and MAA as a Function of Monomer/Water Ratio

MONOMER PARTITION AS A FUNCTION OF DN

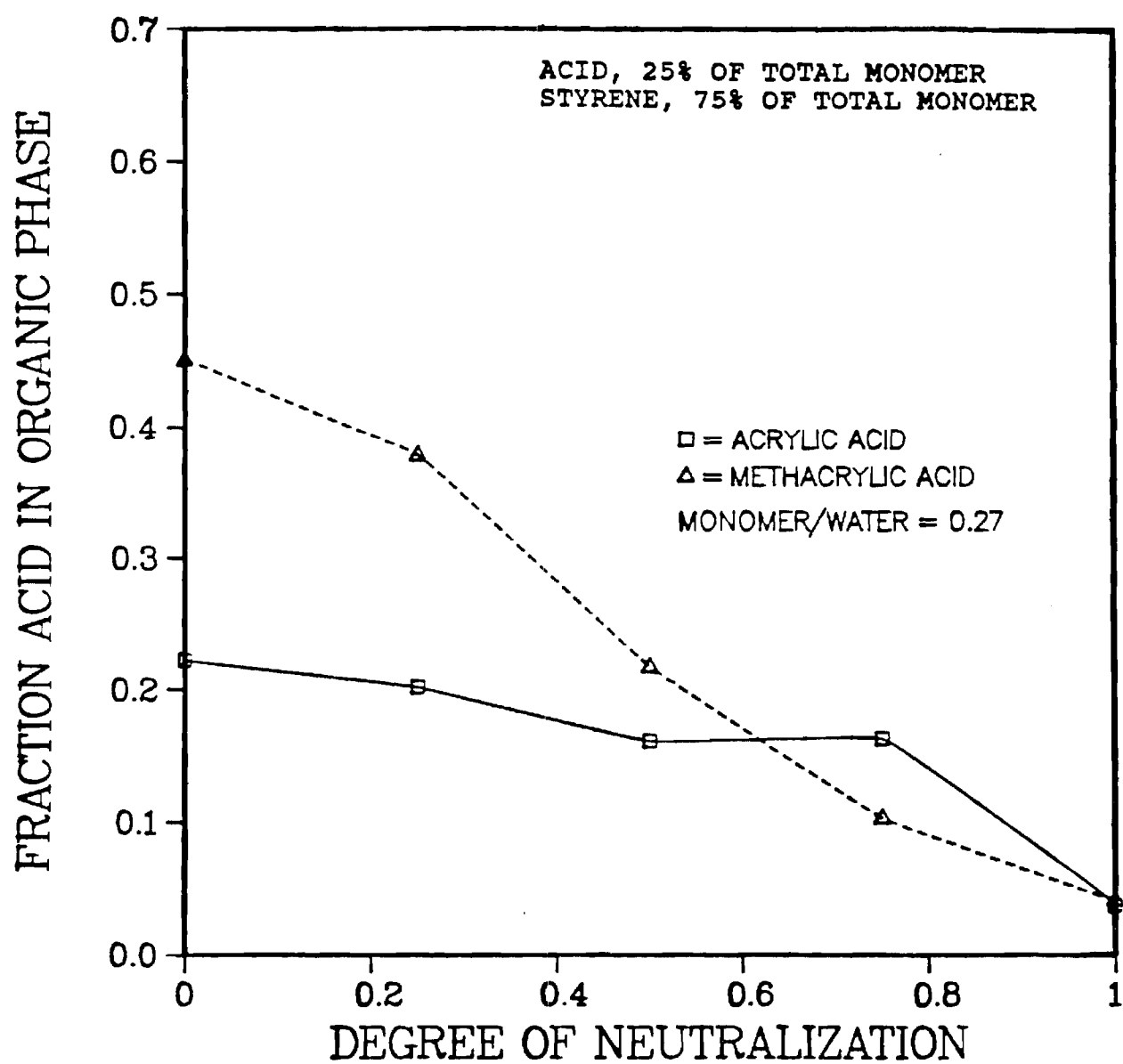


Figure 13 - Monomer Partition of AA and MAA as a Function of DN

present, the MAA is more likely to associate with the organic phase than the AA due to its more hydrophobic nature, or conversely, the water is more likely to solvate the more hydrophilic AA monomer units than the less hydrophilic MAA monomer units.

Figure 13 reveals that the partition of MAA between the two phases is more sensitive to DN than is AA. The fraction of MAA in the organic phase decreases significantly with increasing DN. AA shows only a moderate decrease. The decrease in partition of acid monomer into the particles with increasing DN is due to the electrostatic repulsion between the anionic surfactant molecules (which are aligned along the surface of the particles) and the increased amount of monomer in the dissociated (anionic) form.

Thermodynamic forces control the interactions which exist between monomers with water, particles, droplets, and other monomers. A more involved experimental and theoretical approach is necessary for quantifying these interactions. A description of the approach taken for determining the interactions for AA/styrene and MAA/styrene systems is described in detail in the following section.

Much attention has been given in the literature to the thermodynamic forces which control the partition of monomer(s) between particle, droplet, and aqueous phases in emulsion systems. Morton et. al.[13] showed that the driving force for absorption of monomer by particles (or droplets) is governed by differences in their partial molar free energies. The free energy can be divided into two contributions, free energy of mixing (dG_{mix}) and interfacial free energy (dG_{inter}).

$$dG = dG_{\text{mix}} + dG_{\text{int}} \quad (14)$$

Flory and Huggins [14] presented a lattice theory for prediction of partial molar free energy of mixing component i in phase q for polymer solutions. An interfacial free energy term is added when the phases are finely subdivided as usually occurs in emulsion polymerization systems. Ugelstad [15] proposed that the Flory-Huggins approach may be applied provided the interaction parameters (X_{ij}) and the ratio of equivalent segments (m_{ij}) are obtained experimentally. Equations for the partial molar free energy for all three phases are presented below. [16,17].

(i) monomer droplets

$$(\Delta G/RT)_{1,d} = \ln \phi_{1,d} + (1-m_{12})\phi_{2,d} + X_{12}\phi_{2,d}^2 + 4 \gamma_d \bar{v}_1 / (D_d RT) \quad (15)$$

$$(\Delta G/RT)_{2,d} = \ln \phi_{2,d} + (1-1/m_{12})\phi_{1,d} + X_{12}(1/m_{12})\phi_{1,d}^2 + 4 \gamma_d \bar{v}_2 / (D_d RT) \quad (16)$$

where, ϕ_{iq} = volume fraction of component i in phase q

m_{ij} = ratio of equivalent molecular segments between i
and j often expressed by the ratio of molar
volumes (V_i/V_j)

X_{ij} = interaction parameter between components i and j .

D = diameter

γ = interfacial tension

d = droplet phase ; aq = aqueous phase ; p = particle phase

1 = acid

2 = styrene

P = copolymer

(ii) monomer-polymer particles

$$\begin{aligned}
 (\Delta G/RT)_{1,p} = & \ln \phi_{1,p} + (1-m_{12})\phi_{2,p} + (1-m_{1p})\phi_{p,p} + X_{12}\phi_{2,p}^2 + X_{1,p}\phi_{p,p}^2 \\
 & + (X_{12}+X_{1,p}-m_{12}X_{2,p})\phi_{2,p}\phi_{p,p} + 4 \gamma_p \bar{v}_1 / (D_p RT) \quad (17)
 \end{aligned}$$

$$\begin{aligned}
 (\Delta G/RT)_{2,p} = & \ln \phi_{2,p} + (1-1/m_{12})\phi_{1,p} + (1-m_{2p})\phi_{p,p} + 4 \gamma_p \bar{v}_2 / (D_p RT) \\
 & + 1/m_{12} [X_{12}\phi_{1,p}^2 + m_{12}X_{2,p}\phi_{p,p}^2 + (X_{12}+m_{12}X_{2,p}-X_{1,p})\phi_{1,p}\phi_{p,p}] \quad (18)
 \end{aligned}$$

(iii) aqueous phase

$$\begin{aligned}
 (\Delta G/RT)_{1,aq} = & \ln \phi_{1,aq} + (1-m_{12})\phi_{2,aq} + (1-m_{1w})\phi_{w,aq} + X_{12}\phi_{2,aq}^2 \\
 & + X_{1,w}\phi_{w,aq}^2 + \phi_{2,aq}\phi_{w,aq}(X_{12} + X_{1w} - X_{2,w}m_{12}) \quad (19)
 \end{aligned}$$

If styrene is used as monomer 2, then due to its low solubility (0.5g/L), one may consider $\phi_{2,aq}$ (0.0005) to be negligible relative to the other terms in the equation, thus (19) reduces to (19')

$$(\Delta G/RT)_{1,aq} = \ln \phi_{1,aq} + (1-m_{1w})\phi_{w,aq} + X_{1,w}\phi_{w,aq}^2 \quad (19')$$

Guillot [18] states that a simplified form of the free energy Eq. (20) in the aqueous phase may be written for monomers with low solubility.

$$(\Delta G/RT)_{2,aq} = \ln \phi_{2,aq} \quad (20)$$

However, it is not clear how Guillot obtains this simplification. Therefore, the full form of the free energy equation (20') for styrene in the aqueous phase is used in this work.

$$(\Delta G/RT)_{2, \text{aq}} = \ln \phi_{2, \text{aq}} + (1 - 1/m_{12}) \phi_{1, \text{aq}} + (1 - m_{2, \text{w}}) \phi_{\text{w}, \text{aq}} + X_{12} \phi_{1, \text{aq}}^2 \\ X_{2, \text{w}} \phi_{\text{w}, \text{aq}}^2 + \phi_{1, \text{aq}} \phi_{\text{w}, \text{aq}} (X_{12} + m_{12} X_{2, \text{w}} - X_{1, \text{w}}) \quad (20')$$

A series of material balances may be written for this two monomer system.

(i) phases

$$\phi_{1, \text{p}} + \phi_{2, \text{p}} + \phi_{\text{p}, \text{p}} = 1 \quad \text{polymer particles} \quad (21)$$

$$\phi_{1, \text{d}} + \phi_{2, \text{d}} = 1 \quad \text{droplets} \quad (22)$$

$$\phi_{1, \text{aq}} + \phi_{2, \text{aq}} + \phi_{\text{w}, \text{aq}} = 1 \quad \text{aqueous phase} \quad (23)$$

(ii) components

$$A_0 \bar{V}_1 (1 - X_1) = \phi_{1, \text{p}} V_{\text{p}} + \phi_{1, \text{d}} V_{\text{d}} + \phi_{1, \text{aq}} V_{\text{aq}} \quad \text{acid} \quad (24)$$

$$B_0 \bar{V}_2 (1 - X_2) = \phi_{2, \text{p}} V_{\text{p}} + \phi_{2, \text{d}} V_{\text{d}} + \phi_{2, \text{aq}} V_{\text{aq}} \quad \text{styrene} \quad (25)$$

$$A_0 \bar{V}_{\text{pA}} X_1 + B_0 \bar{V}_{\text{pB}} X_2 + V_{\text{seed}} = \phi_{\text{p}, \text{p}} V_{\text{p}} \quad \text{copolymer} \quad (26)$$

$$W_0 \bar{V}_{\text{w}} = \phi_{\text{w}, \text{aq}} V_{\text{aq}} \quad \text{water} \quad (27)$$

where, A_0 , B_0 , and W_0 are initial ^{moles} masses of acid, styrene, and water, respectively. X_1 and X_2 are mass conversions of acid and styrene, respectively. (\bar{V}_j = molar volume of component j .)

Equilibrium Between Monomer-polymer Particles and the Aqueous Phase

The free energies of all existing phases at equilibrium are equivalent.

$$(\Delta G/RT)_{1,p} - (\Delta G/RT)_{1,aq} = 0 \quad (28)$$

$$\text{Eq. (17)} - \text{Eq. (19)} = 0 \quad (28')$$

$$(\Delta G/RT)_{2,p} - (\Delta G/RT)_{2,aq} = 0 \quad (29)$$

$$\text{Eq. (18)} - \text{Eq. (20')} = 0 \quad (29')$$

Equations (28') and (29') contain a large number of unknown parameters, namely, m_{12} , m_{1w} , $m_{1,p}$, $m_{2,p}$, X_{12} , $X_{1,p}$, $X_{2,p}$, and $X_{1,w}$. Before presenting a method of obtaining these parameters, equilibrium between the aqueous phase and monomer droplets is addressed. The appropriate equations for equilibrium between monomer present in these two phases are as follows.

$$(\Delta G/RT)_{1,aq} - (\Delta G/RT)_{1,d} = 0 \quad (30)$$

$$\text{Eq. (19)} - \text{Eq. (15)} = 0 \quad (30')$$

$$(\Delta G/RT)_{2,aq} - (\Delta G/RT)_{2,d} = 0 \quad (31)$$

$$\text{Eq. (20')} - \text{Eq. (16)} = 0 \quad (31')$$

Additional unknown parameters are χ_d and D_d . Experimental determination of most of these parameters is necessary as noted by Ugelstad [15]. Because of the large number of unknown parameters, simplifications in these equations, and thus simplification of the experiments needed to obtain these parameters was pursued.

A first step is modification of Eq. (28') to produce Eq. (28'') for the limiting case that $\phi_{2,p} = 0$ (i.e. only acid monomer is added to a mixture of polymer particles).

$$\ln \phi_{1,p} + (1 - m_{1,p})\phi_{p,p} + X_{1,p}\phi_{p,p}^2 + 4 \chi_p \bar{V}_1 / (D_p RT) \\ - [\ln \phi_{1,aq} + (1 - m_{1,w})\phi_{w,aq} + X_{1,w}\phi_{w,aq}^2] = 0 \quad (28'')$$

The unknown parameters are then $X_{1,p}$, $m_{1,w}$, $X_{1,w}$, and $m_{1,p}$. Since the ratio of molecular segments for a monomer and polymer is usually very small, a common assumption is that $m_{1,p}$ (and $m_{2,p}$) = 0. The ratio of molar volumes for the acid and water can be used as a reasonable estimate of $m_{1,w}$. The remaining two parameters are then $X_{1,p}$ and $X_{1,w}$, and these were fitted to experimental data using Eq. (28'').

Experimental data were generated by adding various amounts of acid to a mixture of seed particles, mixing for at least 30 minutes, separating the aqueous and particle phases (filtration), and subsequent measurement of the acid remaining in the aqueous phase (titration).

This was repeated for various monomer/seed ratios for both MAA and AA monomers. The partition of acid monomer between the aqueous and particle phases determined from these experiments is shown in Figures 14 and 15 for AA and MAA, respectively.

The two-monomer interaction parameter, X_{12} , was obtained by repeating the above experiments with the addition of various amounts of styrene for each quantity of acid added, then fitting the data with Eq. (28'). The ratio of molar volumes of the two monomers were used to estimate m_{12} . Care was taken not to add styrene in sufficient amount so as to form droplets since Eq. (14') does not apply if droplets are present. Data from Jansson [19] provided estimates of the maximum amounts of monomer which could be added so as to swell the particles without forming droplets. It was also assumed that all of the styrene added was present in the particles since its solubility in water is very low (0.5g/L)^[12]. Values for the fitted parameters obtained from the experimental data are listed in Table 5.

The fitted parameters can then be substituted into Eqs. (21) - (31). Solution of this system of 11 independent equations gives the partition of the monomer (for the case of Interval II) between the three phases via the following 11 dependent variables: $\phi_{1,p}$, $\phi_{2,p}$, $\phi_{p,p}$, $\phi_{1,d}$, $\phi_{2,d}$, $\phi_{1,aq}$, $\phi_{2,aq}$, $\phi_{w,aq}$, V_p , V_d , and V_{aq} .

The number of equations is reduced to 8 for the case of Interval III in which case no droplets are present. The following 8 dependent variables may then be calculated for this case: $\phi_{1,p}$, $\phi_{2,p}$, $\phi_{p,p}$, $\phi_{1,aq}$, $\phi_{2,aq}$, $\phi_{w,aq}$, V_p , and V_{aq} .

AA PARTITION DATA W/RAP 139 PARTICLES

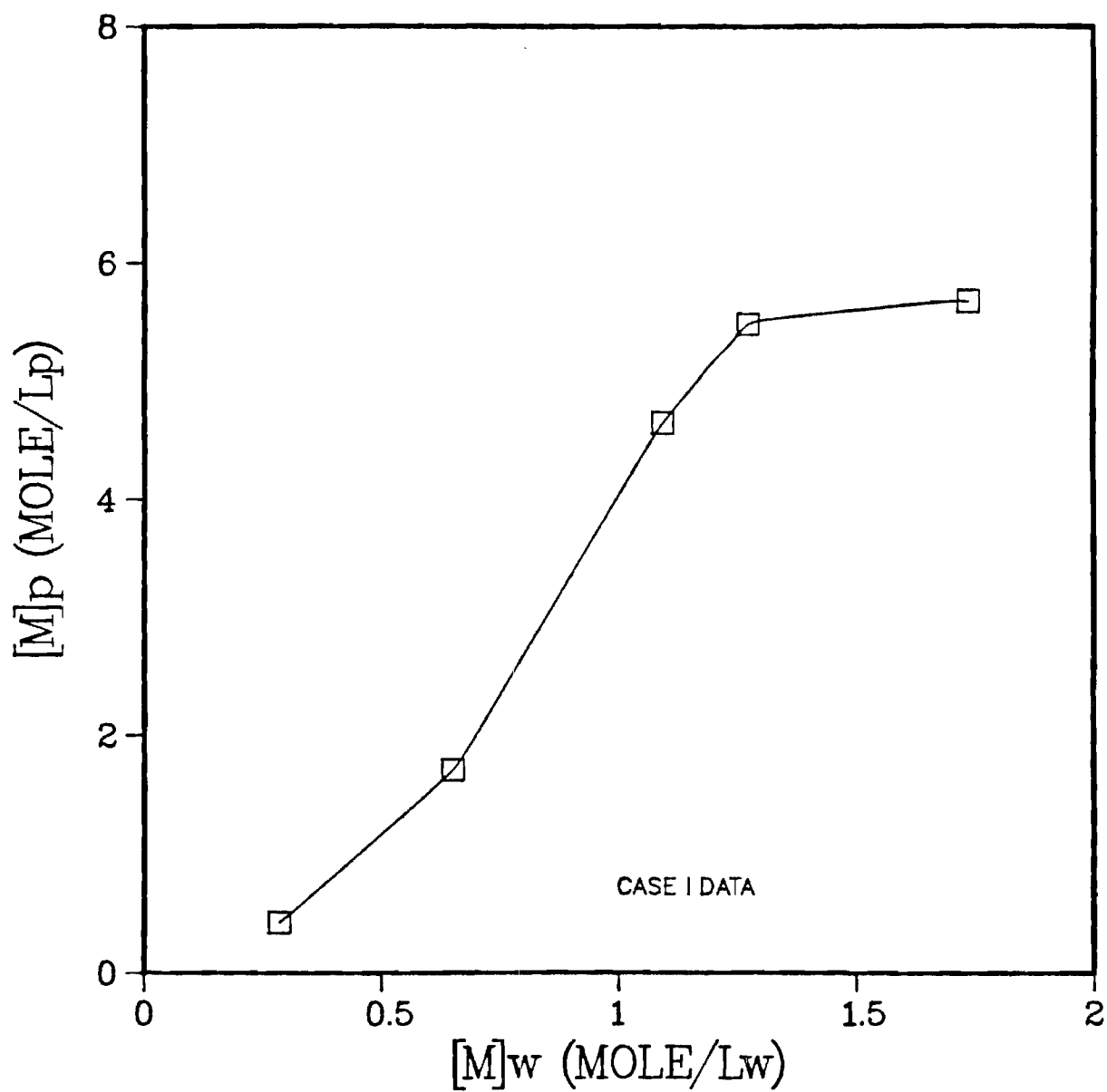


Figure 14 - Partition of AA Between Aqueous and Particle Phases

MAA PARTITION W/ RAP 139 SEED PARTICLES

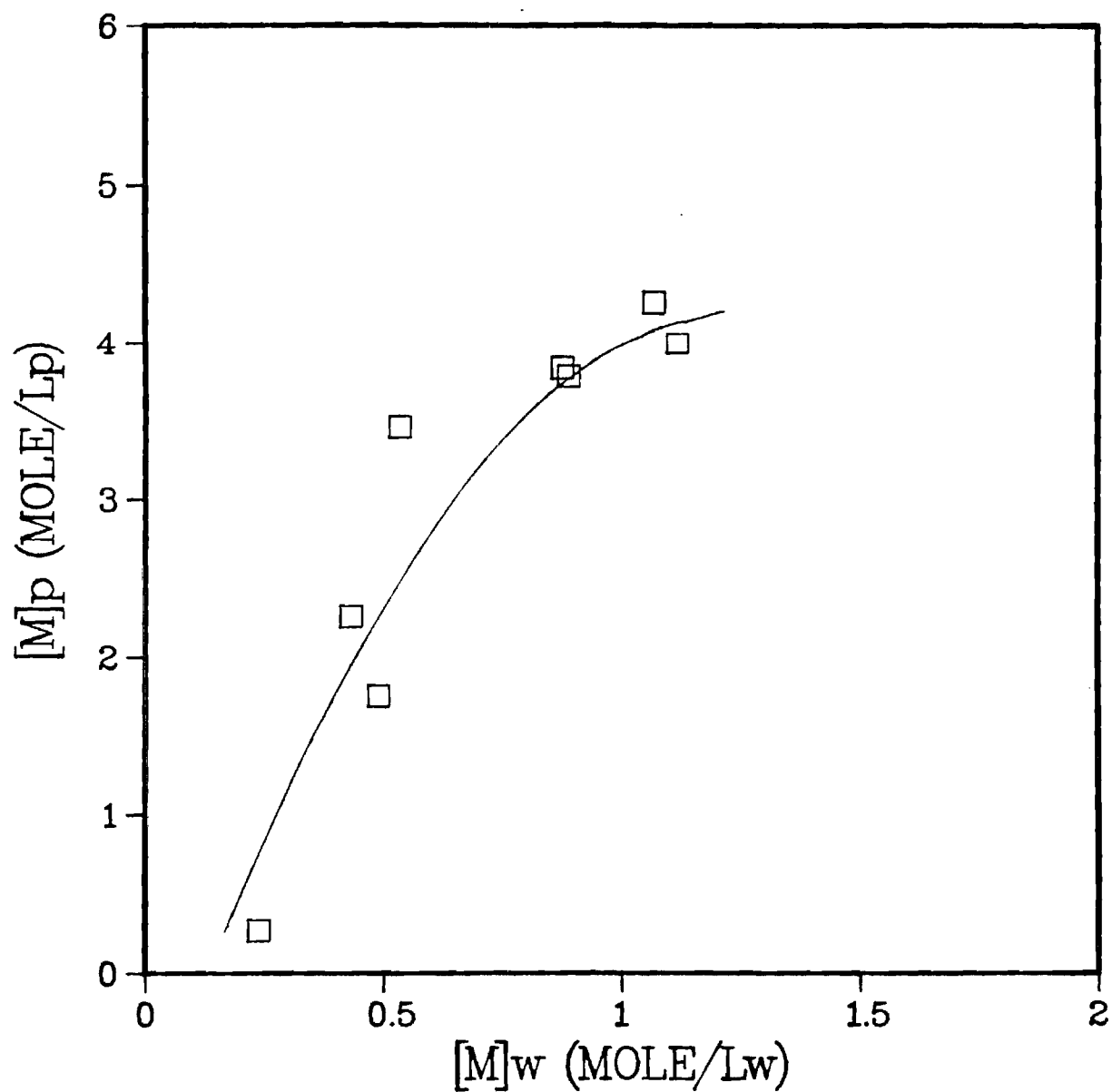


Figure 15 - Partition of MAA Between Aqueous and Particle Phases

There are four independent variables which depend directly on the recipe, namely A_0 , B_0 , W_0 , and V_{seed} .

A check of the fitted parameters was made by substituting the values into the series of 8 equations with 8 unknowns, solving for the unknown values, and comparing these values to the experimentally measured ones. The entire series of 11 equations with 11 unknowns does

Table 5 - Fitted Parameters Obtained from Monomer Partition Experiments

	AA	MAA
$X_{1,p}$	2.287	2.911
$X_{1,w}$	6.720	8.176
$X_{1,2}$	0.507	0.538
Values of other parameters used:		
$m_{1,w}^*$	3.816	4.705
$m_{1,2}^*$	0.597	0.735
$X_{2,w}$	17.5	17.5

$$\begin{aligned} X_{2,p} &= 0.5 \\ \gamma_p &= 5.0 \times 10^{-3} \text{ N/m} \end{aligned}$$

* Equal to the ratio of the molar volumes of each component

not apply since the partition experiments were designed to avoid droplet formation. Typical results are shown below in Table 6 for MAA and AA in which the experimental value, denoted by EXP, is compared to the calculated value, denoted by X, based on the fitted parameters. A

check on additional experimental data was made, and similar agreement between the experimental and calculated values was obtained. (The value for $X_{2,w}$ was not obtained directly from the experimental data. It was estimated then adjusted to give the best fit of EXP and X. The value of 17.5 gave the best fit independent of whether MAA or AA data were used.)

Table 6 - Comparison of Experimental and Calculated Monomer Partition Data

	MAA (5.0 ml) Styrene (1.0 ml)		AA (5.0 ml) Styrene (1.0 ml)	
	EXP	X	EXP	X
$\phi_{1,p} =$	0.1611	0.1474	0.1348	0.1237
$\phi_{2,p} =$	0.1013	0.1030	0.1045	0.1058
$\phi_{p,p} =$	0.7376	0.7496	0.7607	0.7705
$\phi_{1,aq} =$	0.0385	0.0402	0.0418	0.0431
$\phi_{2,aq} =$	0.0005	0.0000031	0.0005	0.0000031
$\phi_{w,aq} =$	0.9610	0.9598	0.9577	0.9569
$V_p(mL) =$	9.868	9.708	9.568	9.445
$V_{aq}(mL) =$	88.535	88.694	88.835	88.957

The close match to the calculated and experimental values suggests that the fitted interaction parameters are reasonable. The only value which appears to show significant disagreement is $\phi_{2,aq}$. This value is the volume fraction of styrene in the aqueous phase and was the only parameter not determined experimentally. The value reported was obtained from literature [12].

Emulsion Copolymerization Model

Aqueous-Phase Free Radical Concentration in Emulsion Copolymerization Systems

Emulsion copolymerization with at least one monomer which has a high degree of water-solubility probably involves a significant amount of polymerization in the aqueous phase. A kinetic model for emulsion copolymerization of these types of systems requires that the concentration of free radicals in the aqueous phase be known. A useful expression for obtaining the aqueous phase free-radical concentration can be derived by the following method.

Reactions affecting all water phase radical species are listed in Table 7. Corresponding rate expressions are also listed. An expression for the rate of change of initiator free radical species can be written as follows:

$$\begin{aligned}
 d[I^*]/dt = & \text{rate of formation (decomposition of } I_2) - \text{rate of monomer initiation} - \text{rate of termination w/ other } I^* \text{ radicals} \\
 & - \text{rate of termination w/ oligomer radicals} - \text{rate of capture by particles} + \text{rate of desorption from particles} \\
 & - \text{rate of capture by monomer droplets} - \text{rate of capture by micelles} \quad (32)
 \end{aligned}$$

Due to the high concentration of monomer relative to the concentration of initiator radicals, it is unlikely that termination

Table 7 - Reactions Affecting Water Phase Radical Species

1. decomposition	$I_2 \xrightarrow{k_d} 2I^*$	$R_d = 2fk_d[I_2]$
2a. monomer initiation	$I^* + A_w \xrightarrow{k_{IA}} R_{1A}^*$	$R_{IA} = k_{IA}[A]_w[I^*]$
2b.	$I^* + B_w \xrightarrow{k_{IB}} R_{1B}^*$	$R_{IB} = k_{IB}[B]_w[I^*]$
3. deactivation	$I^* + \text{impurities} \rightarrow \text{inactive products}$	$R_{deac} = 2(1-f)k_d[I_2]$
4a. termination	$I^* + I^* \xrightarrow{k_{twII}} I_2$	$R_{twII} = k_{twII} [I^*]^2$
4b.	$I^* + R_{jA}^* \xrightarrow{k_{twIA}} I-R_{jA}$	$R_{term} = ([R_{jA}^*]k_{twIA} + [R_{jB}^*]k_{twIB}) [I^*]$
4c.	$I^* + R_{jB}^* \xrightarrow{k_{twIB}} I-R_{jB}$	
		$= \bar{k}_{twI} [R_{tot}] [I^*]$
5a. propagation	$R_{jA}^* + A_w \xrightarrow{k_{pAA}} R_{j+1A}^*$	$R_{pAA} = k_{pAA}[R_{jA}^*][A]_w$
5b. (j=1 to j _{cr} -1)	$R_{jA}^* + B_w \xrightarrow{k_{pAB}} R_{j+1B}^*$	$R_{pAB} = k_{pAB}[R_{jA}^*][B]_w$
5c.	$R_{jB}^* + A_w \xrightarrow{k_{pBA}} R_{j+1A}^*$	$R_{pBA} = k_{pBA}[R_{jB}^*][A]_w$
5d.	$R_{jB}^* + B_w \xrightarrow{k_{pBB}} R_{j+1B}^*$	$R_{pBB} = k_{pBB}[R_{jB}^*][B]_w$
6a. capture of initiator and oligomer radicals	$I^* + P \xrightarrow{k_{CI}} P_I^*$	$R_{CI} = k_{CI}N_p[I^*]$
6b.	$R_{jA}^* + P \xrightarrow{k_{CjA}} P_A^*$	$R_{CA} = k_{CjA}N_p[R_{jA}^*]$
6c. by particles	$R_{jB}^* + P \xrightarrow{k_{CjB}} P_B^*$	$R_{CB} = k_{CjB}N_p[R_{jB}^*]$
7a. desorption of radicals from particles	$P_I^* \xrightarrow{k_{desI}} I^* + P$	$R_{desI} = k_{desI}(N_p \bar{n}/N_A)$
7b. particles	$P_A^* \xrightarrow{k_{desA}} R_{jA}^* + P$	$R_{des} = \bar{k}_{des}(N_p \bar{n}/N_A)$ where
		$\bar{k}_{des} \bar{n} N_p = (k_{desA} n_A + k_{desB} n_B) N_p$

Table 7 (continued)

7c.	$P_{B^*} \xrightarrow{k_{desB}} R_{jB^*} + P$	
8a. termination w/ oligomer radicals	$R_{iA^*} + R_{jA^*} \xrightarrow{k_{twAA}} O_{i+j}$ where $\bar{k}_{tw} = 1/(1+L_w)(k_{twAA} + L_w k_{twAB} + L_w^2 k_{twBB})$	$R_{term} = \bar{k}_{tw} [R_i^*] [R_{tot}^*]$
8b.	$R_{iA^*} + R_{jB^*} \xrightarrow{k_{twAB}} O_{i+j}$	
8c.	$R_{iB^*} + R_{jB^*} \xrightarrow{k_{twBB}} O_{i+j}$	
9a. capture of initiator and oligomer	$I^* + D \xrightarrow{k_{CDI}} P_{DI}^*$	$R_{CDI} = k_{CDI} N_D [I^*]$
9b. by monomer drops	$R_{jA^*} + D \xrightarrow{k_{CDA}} P_{DA}^*$	$R_{CDA} = k_{CDA} N_D [R_{jA}^*]$
9c.	$R_{jB^*} + D \xrightarrow{k_{CDB}} P_{DB}^*$	$R_{CDB} = k_{CDB} N_D [R_{jB}^*]$
10a. capture of initiator and oligomer	$I^* + M_C \xrightarrow{k_{McI}} P_{MI}^*$	$R_{McI} = k_{McI} N_{Mc} [I^*]$
10b. radicals by micelles	$R_{jA^*} + M_C \xrightarrow{k_{McA}} P_{MA}^*$	$R_{McA} = k_{McA} N_{Mc} [R_{jA}^*]$
10c.	$R_{jB^*} + M_C \xrightarrow{k_{McB}} P_{MB}^*$	$R_{McB} = k_{McB} N_{Mc} [R_{jB}^*]$

* Chain Transfer reactions in the aqueous phase may also be included. However, they do not change the total number of radicals, $[R_{tot}^*]$, in the aqueous phase. They only change the identity of the radical species from A* to B* or vice versa. Since only $[R_{tot}^*]$ is needed in the model, chain transfer reactions are not included in Table 7.

between two initiator radicals will occur. The initiator free radical is very reactive and has a short life-time. Therefore, the third and last four terms may be neglected. The resulting expression is given by Eq. (33).

$$d[I^*]/dt = 2fk_d[I_2] - [k_{IA}[A]_w + k_{IB}[B]_w][I^*] - k_{twI}[R_{tot}][I^*] \quad (33)$$

A balance on the monomer radicals ($j=1$) is given by Eq. (34).

$$\begin{aligned} d[R^*]/dt = & \text{rate of initiation} - \text{rate of formation} - \text{rate of termination} \\ & \text{of monomer molecules} \quad \text{of } j=2 \text{ mers} \quad \text{w/ initiator radicals} \\ & - \text{rate of termination} - \text{rate of capture} - \text{rate of capture} \nearrow \\ & \text{w/ oligomer radicals} \quad \text{by particles} \quad \text{monomer drops, micelles} \\ & + \text{rate of desorption} \\ & \text{from particles} \end{aligned} \quad (34)$$

Capture by monomer droplets is usually negligible, and if the surfactant level is kept below its critical micelle concentration, micelles will not be present in the system. Applying the assumption that the identity of a radical A^* or B^* is independent of chain length gives,

$$R_{1A} = R_1/(1 + I_w) \quad (35a)$$

$$\text{and} \quad R_{1B} = I_w R_1/(1 + I_w). \quad (35b)$$

The rate expression can then be written by Eq. (36).

$$\begin{aligned} d[R_1^*]/dt = & (k_{IA}[A]_w + k_{IB}[B]_w)[I^*] - R_1^*/(1+I_w) [(k_{pAA}+I_w k_{pBA})[A]_w \\ & + (k_{pAB}+I_w k_{pBB})[B]_w] - \bar{k}_{twI}[R_1^*][I^*] - \bar{k}_{tw}[R_1^*][R_{tot}^*] \\ & - \bar{k}_{c1}[R_1^*]N_p + k_{des}(N_p \bar{n}/N_a) \end{aligned} \quad (36)$$

where

$$\bar{k}_{twI} = \frac{[R_{jA}^*]k_{twIA} + [R_{jB}^*]k_{twIB}}{[R_{jA}^*] + [R_{jB}^*]}$$

$$R_{tot} = \sum_{j=1}^{j_{cr}} R_j = \sum_{j=1}^{j_{cr}} R_{jA} + R_{jB}$$

$$\bar{k}_{tw} = 1/(1 + L_w)^2 (k_{twAA} + L_w k_{twAB} + L_w^2 k_{twBB})$$

$$\bar{k}_{c1} = \frac{k_{c1A}[R_{1A}^*] + k_{c1B}[R_{1B}^*]}{[R_{1A}^*] + [R_{1B}^*]}$$

and L_w is a term introduced by Nomura which assumes that the probability of a radical ending with an A* or B* unit is independent of chain length, and that the change in the proportion of the radicals is small over the course of the reaction period. Then L_w can be defined by

$$L_w = [R_{jB}^*]/[R_{jA}^*] = k_{pAB}[B]_w/(k_{pBA}[A]_w)$$

Next, a balance is written on the j mer radicals with $j > 1$.

$$\begin{aligned} d[R_j^*]/dt = & \text{rate of formation of } j \text{ mer} - \text{rate of formation of } j+1 \text{ mer} - \text{rate of termination w/ initiator radicals} \\ & - \text{rate of termination w/ oligomer radicals} - \text{rate of capture by particles} - \text{rate of capture by drops, micelles} \\ & + \text{rate of desorption from particles} \end{aligned} \quad (37)$$

Again, capture by droplets and micelles can be neglected relative to capture by seed particles. Desorption from latex particles is also unlikely if j is much larger than one. The resulting rate expression is given by Eq.(38). (Note that Eq.(35) has been extended to include radicals of length j.)

$$\begin{aligned}
d[R_j^*]/dt = & [R_j^*]/(1+L_w) [k_{pAA}+L_w k_{pBA}][A]_w + (k_{pAB}+L_w k_{pBB})[B]_w \\
& - [R_{j+1}^*](1+L_w) [k_{pAA}+L_w k_{pBA}][A]_w + (k_{pAB}+L_w k_{pBB})[B]_w \\
& - \bar{k}_{twI}[R_j^*][I^*] - \bar{k}_{tw}[R_j^*][R_{tot}^*] - \bar{k}_{Cj}[R_j^*]N_p \quad (38)
\end{aligned}$$

where,

$$\bar{k}_{Cj} = \frac{k_{CjA}[R_{jA}^*] + k_{CjB}[R_{jB}^*]}{[R_{jA}^*] + [R_{jB}^*]}$$

$$[R_j^*] = [R_{jA}^*] + [R_{jB}^*]$$

The steady state assumption must be applied in order to solve the j_{cr} system of equations. The derivatives are all set to zero and the j_{cr} equations are summed yielding Eq. (39).

$$\begin{aligned}
2fk_d[I_2] - 2\bar{k}_{twI}[R_{tot}^*][I^*] - \bar{k}_{tw} \sum_{j=1}^{j_{cr}} [R_j^*][R_{tot}^*] - N_p \sum_{j=1}^{j_{cr}} \bar{k}_{Cj}[R_j^*] \\
+ k_{des}(N_p n/N_A) \\
- [R_{j_{cr}-1}^*]/(1+L_w) [(k_{pAA} + L_w k_{pBA})[A]_w + (k_{pAB} + L_w k_{pBB})[B]_w] = 0 \quad (39)
\end{aligned}$$

One may then define \bar{k}_C , an average radical capture constant, as was done by Ugelstad,

$$\bar{k}_C = \sum_{j=1}^{j_{cr}} k_{Cj}[R_j^*]/R_{tot}$$

and rewrite the expression for the average termination constant,

$$\bar{k}_{tw} \sum_{j=1}^{j_{cr}} [R_j^*][R_{tot}^*] = \bar{k}_{tw}[R_{tot}^*]^2$$

A more simplified equation then follows:

$$2fk_d[I_2] - 2\bar{k}_{tw}[R_{tot}^*][I^*] - \bar{k}_{tw}[R_{tot}^*]^2 - \bar{k}_{cN_p}[R_{tot}^*] + k_{des}(N_p \bar{n}/N_A) - [R_{jcr-1}^*]/(1+L_w) [(k_{pAA} + L_w k_{pBA})[A]_w + (k_{pAB} + L_w k_{pBB})[B]_w] = 0 \quad (40)$$

This equation is of the same form as that derived by Ugelstad for homopolymerization. Several additional assumptions can be made to simplify this expression.

1. Since seeds are present, flocculation of oligomers onto seed particles should be great enough that few oligomer species can reach the critical chain length needed for homogeneous nucleation of particles. Therefore, $[R_{jcr-1}^*]$ should be very small (especially compared to $[R_{tot}^*]$), and the last term can be neglected.

2. Since the initiator is so reactive, and the concentration of monomer in the aqueous phase is high (due to the high water-solubility of the acid monomers used in this study), $[I^*]$ should be small, and the second term can be neglected.

These simplifications lead to Eq. (41).

$$2fk_d[I_2] - \bar{k}_{tw}[R_{tot}^*]^2 - \bar{k}_{cN_p}[R_{tot}^*] + k_{des}(N_p \bar{n}/N_A) = 0 \quad (41)$$

Application of the quadratic formula leads to a direct solution for $[R_{tot}^*]$.

$$[R_{tot}^*] = \frac{\sqrt{(\bar{k}_{cN_p})^2 + 4\bar{k}_{tw}(k_{des}(N_p \bar{n}/N_A) + 2fk_d[I_2])} - \bar{k}_{cN_p}}{2\bar{k}_{tw}} \quad (42)$$

Extension to Rate Expression for Diffusion-Controlled Aqueous-Phase Copolymerization

The rationale used in the previous derivation of $[R_{\text{tot}}^*]$ can be used in deriving an expression for diffusion-controlled aqueous phase copolymerization in an emulsion system. The rate expression is given by Eq. (43).

$$R_{\text{paq}} = - (d[A] + d[B])/dt = k_{AA}[A^*]_w[A]_w + k_{AB}[A^*]_w[B]_w + k_{BB}[B^*]_w[B]_w + k_{BA}[B^*]_w[A]_w \quad (43)$$

A steady-state concentration is assumed for each type of radical.

$$k_{BA}[B^*]_w[A]_w = k_{AB}[A^*]_w[B]_w \quad (44)$$

Steady-state is also assumed for the total concentration of radicals which normally leads to an expression of the form

$$R_{\text{initiation}} = R_{\text{termination}} \quad (45)$$

However, as shown in the previous discussion involving an emulsion system, radical capture by latex particles and radical desorption from latex particles are important. Therefore, Eq. (45) must be modified:

$$R_{\text{initiation}} = R_{\text{termination}} + R_{\text{capture}} - R_{\text{desorption}} \quad (45')$$

which leads to Eq. (46).

$$R_i = 2k_{tAB}([A^*]_w + [B^*]_w)^2 + \bar{k}_c([A^*]_w + [B^*]_w)N_p - k_{des}(N_p \bar{n}/N_A) \quad (46)$$

Rearranging and solving for the free radical concentration gives

$$[A^*]_w + [B^*]_w = [R_{tot}^*]_w = \frac{\sqrt{(\bar{k}_c N_p)^2 + 4(2k_{tAB}(R_i + k_{des}(N_p \bar{n}/N_A)))} - \bar{k}_c N_p}{4 k_{tAB}} \quad (46')$$

where $2k_{tab} = \bar{k}_{tw}$ used in Eq. (42).

Solving for $[B^*]_w$ from equation Eq. (44),

$$[B^*]_w = k_{AB} [A^*]_w [B]_w / (k_{BA} [A]_w) \quad (47)$$

and plugging into Eq. (46') and rearranging gives

$$[A^*]_w = \frac{\sqrt{(\bar{k}_c N_p)^2 + 8k_{tAB}(R_i + k_{des}(N_p \bar{n}/N_A)))} - \bar{k}_c N_p}{4k_{tAB} (1 + k_{AB}[B]_w / (k_{BA}[A]_w))} \quad (48)$$

Combining Eq. (47) and Eq. (48) and substituting into Eq. (43) leads to Eq. (49). First, however, define $Z = [A^*]_w$ given by Eq. (48). Then,

$$R_{paq} = k_{AA}[A]_w Z + k_{AB}[B]_w Z + k_{BB}[B]_w (k_{AB}/k_{BA}) [B]_w / [A]_w Z + k_{AB}[B]_w Z \quad (49)$$

Let $r_A = k_{AA}/k_{AB}$, and $r_B = k_{BB}/k_{BA}$, then

$$R_{paq} = (k_{AA}[A]_w + 2k_{AB}[B]_w + k_{BB}r_B[B]_w^2/[A]_w) Z \quad (49')$$

Substitution for Z and appropriate rearrangement leads to Eq. (49").

$$R_{p\ aq} = \frac{(\sqrt{(\bar{k}_c N_p)^2 + 8k_{tAB}(R_i + k_{des}(N_p \bar{n}/N_A))} - \bar{k}_c N_p)}{4k_{tAB}(r_A[A]_w/k_{AA} + r_B[B]_w/k_{BB})} \times (r_A[A]_w^2 + 2[A]_w[B]_w + r_B[B]_w^2) \quad (49'')$$

The overall emulsion copolymerization model then takes the form:

$$R_{p\ tot} = R_{p\ Ap} + R_{p\ Bp} + R_{p\ aq} \quad (50)$$

where the equations for rates of reaction in the particles are given by Nomura.

$$R_{p\ Ap} = -d[A]_p/dt = [k_{pAA}(1/(1+A)) + k_{pBA}(A/(1+A))] [A]_p(N_p \bar{n}/N_A) \quad (51)$$

$$R_{p\ Bp} = -d[B]_p/dt = [k_{pBB}(A/(1+A)) + k_{pAB}(1/(1+A))] [B]_p(N_p \bar{n}/N_A) \quad (52)$$

$$\text{and } A = \bar{n}_B/\bar{n}_A = (k_{pAA}/k_{pBB}) (r_B/r_A) ([B]_p/[A]_p)$$

Initial Emulsion Copolymerization Reactions with MAA/Styrene and
AA/Styrene

Initial emulsion copolymerization reactions with AA/styrene and MAA/styrene have been run under seeded conditions and with the concentration of surfactant above the critical micelle concentration. (See Table 8 for the recipes used.) Conversion transients for

Table 8 - Recipes for Initial Emulsion Copolymerization Runs

	<u>STAA3</u> (grams)	<u>STYMAA1</u> (grams)
Acid	40	40
Styrene	160	160
Water	606	617
Initiator	1.35	1.35
Seed - RAP 139* (29% polymer, 7% SDS)	143	133

* The surfactant (SDS) used in the runs was that already present in the seed latex.

overall and individual monomer conversions are shown for AA/styrene and MAA/styrene in Figures 16 and 17, respectively. Since the surfactant concentration exceeded the critical micelle concentration, new particle generation probably occurred. The AA, reacted less rapidly than styrene despite the fact that it has a much higher propagation constant. Styrene's faster reaction rate is attributed to its high concentration inside the particles. The MAA, however, reacted faster than styrene even though its propagation constant is less than that of

STAA3 - SEEDED EMULSION COPOLYMERIZATION

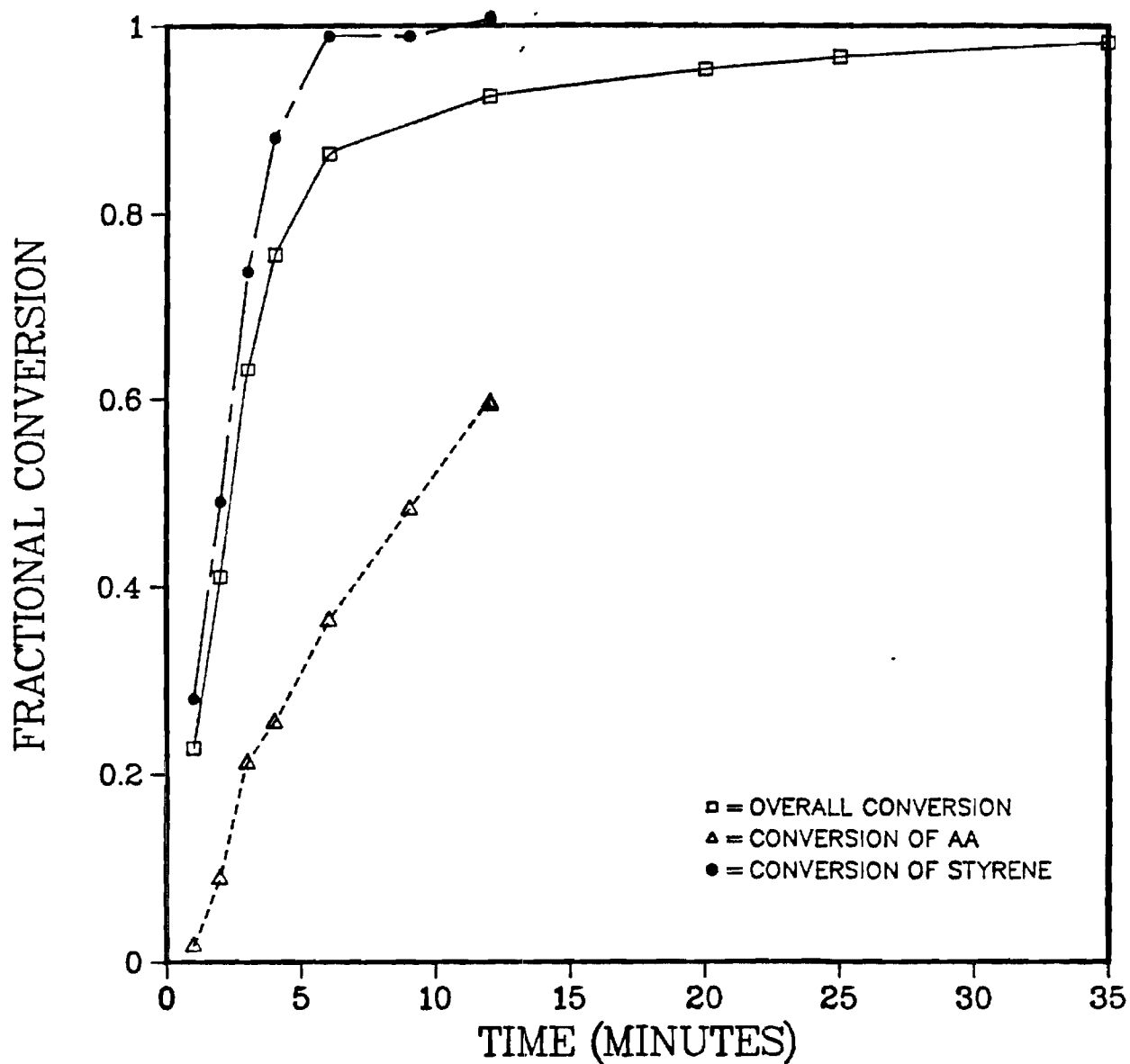


Figure 16 - Conversion Data for AA/Styrene Seeded Emulsion Copolymerization

STYMAA1 EXPERIMENTAL CONVERSION DATA

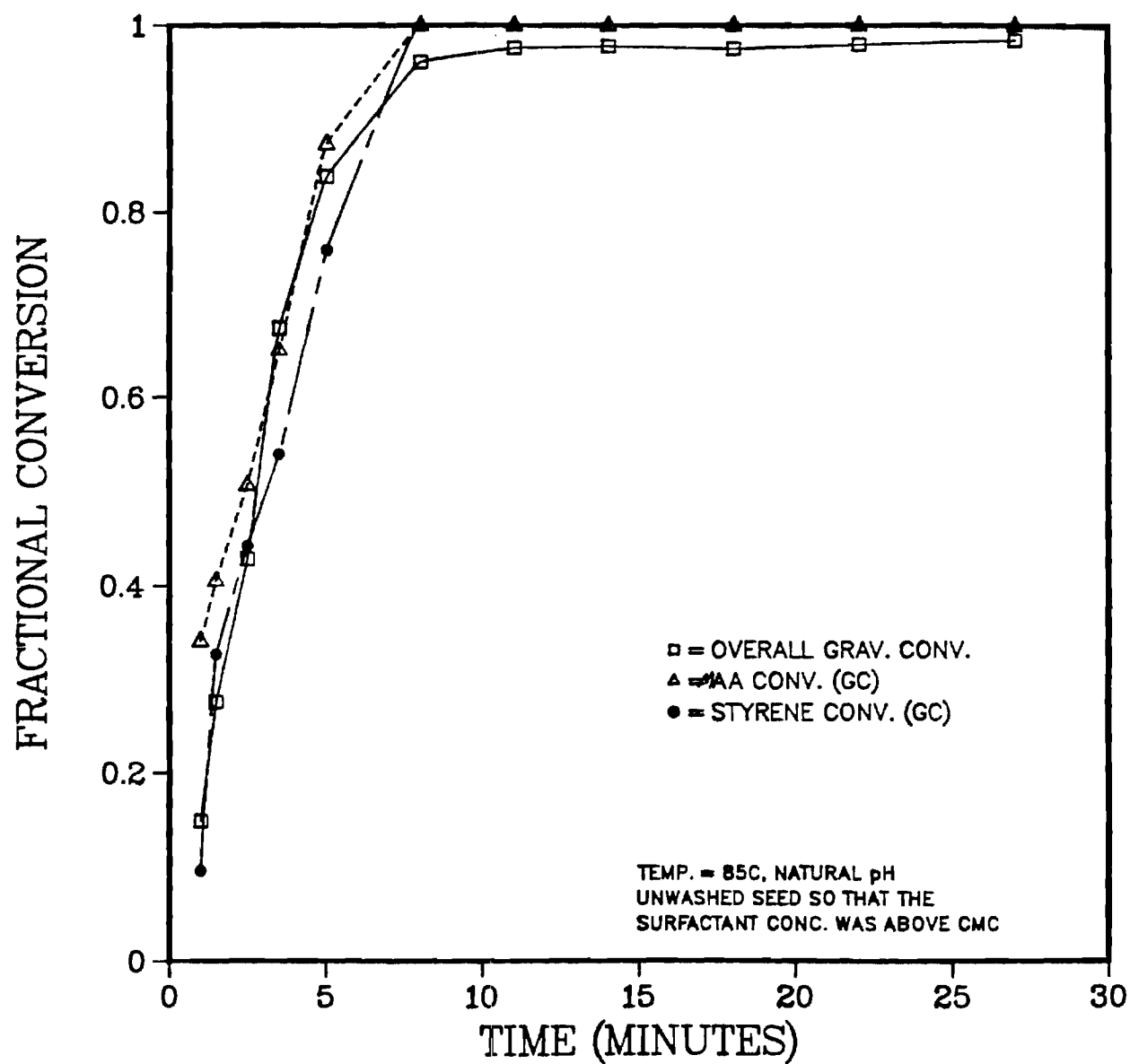


Figure 17 - Conversion Data for MAA/Styrene Seeded Emulsion Copolymerization

AA. MAA partitions more into the particles than does AA such that its concentration in the particles, like that of styrene, is relatively high compared to AA. These results amplify the importance of understanding how the individual monomers partition between the various phases before attempting to predict reaction rates.

Future Work

Future work will include a series of seeded copolymerization reactions with surfactant concentrations below the critical micelle concentration. Individual monomer conversions, partition of monomers, particle sizes, and molecular weights will be measured for samples collected over the conversion period. Additional investigations utilizing nuclear magnetic resonance and spectrophotometry will be conducted to better understand the molecular structure of the copolymer and hopefully determine the critical chain length needed for primary particle formation. Emulsion copolymerization reactions will also be conducted at various DN to better understand the role of the anionic form of the acid monomer in the acid/styrene reactions. Efforts at modeling these reactions will also be continued. Further work involving the solution polymerization of AA may also be necessary in order to determine an adequate expression to use in the emulsion copolymerization model which accounts for the propagation reaction of this monomer with itself.

References

1. J. Brandup and I. Immergut, Polymer Handbook, 2nd Ed., John Wiley and Sons, NY (1975).
2. I. M. Kolthoff and I. K. Miller, American Chem. Soc. J., 73, 3055 (1951).
3. A. I. Yurzhenko and O. P. Brazhnikova, J. Gen. Chem. USSR, 26, 1481 (1956).
4. V.F. Gromov, N.I. Galperina, T. O. Osmanov, O. M. Khomikovskii, and A.D. Abkin, Eur. Poly. J., 16, 529 (1980).
5. N. I. Galperina, T. A. Gugunave, V. F. Gromov, P. M. Khomikovskii, and A. D. Abkin, Vysokomol. Soyed., 17, 1455 (1975).
6. G. C. Pimentel and A. L. McClellan, The Hydrogen Bond, Freeman, San Francisco (1960).
7. D. Chapman, J. Chem. Soc., 225 (1956).
8. J. C. Davis and K. S. Pitzer, J. Phys. Chem., 64, 1886 (1960).
9. E. Constant and A. Lebrun, J. Chim. Phys., 59, 1233 (1962).
10. A. Chapiro and J. Dulieu, Eur. Poly. J., 13, 563 (1977).
11. N. Massif, Ph.D. Thesis, Univ. of Bordeaux (1973).
12. G. W. Poehlein, in Emulsion Polymerization, I. Piirma, Ed., Academic Press, NY, 357 (1982).
13. M. Morton, S. Kaizerman, and M. W. Altier, J. Colloid Sci., 9, 300 (1959).
14. P. J. Flory, Principles of Polymer Chemistry, Cornell Univ. Press, NY (1953).
15. J. Ugelstad, P. C. Mork, H. R. Mfutakamba, E. Soleimany, I. Nordhuus, K. Nustad., R. Schmid, A. Berge, T. Ellingsen, and O. Aune, in Sci. and Tech. of Polymer Colloids, G. W. Poehlein, R. H. Ottewill, J. W. Goodwin, Eds., NATO ASI Ser. Vol. I, 51 (1983).
16. J. Delgado, M.S. El-Aasser, C. Silebi, J. W. Vanderhoff, and J. Guillot, unpublished, Lehigh University - Emulsion Polymers Inst., Bethlehem, PA (1987).
17. W. R. Krigbaum and D. K. Carpenter, J. Poly. Sci., XIV, 241 (1954).
18. J. Guillot, Acta Polymerica, 32, 593 (1981).

19. L. Jansson, "Swelling and Polymerization of Latex Particles", MS Thesis, Georgia Institute of Technology, Atlanta, GA (1983).

BATCH EMULSION COPOLYMERIZATION WITH CARBOXYLIC ACIDS

Progress Report 2

Period: 11/87 - 3/88

GLENN L. SHOAF

Directed by DR. GARY W. POEHLEIN

Georgia Institute of Technology

Atlanta, Georgia 30332

Corporate Sponsor : DOW CHEMICAL

Midland, Michigan

Introduction

Progress on the PhD thesis research entitled "Batch Emulsion Copolymerization with Carboxylic Acids" is presented in the following report for the period 11/87 through 3/88. Topics discussed in the report include kinetic data for seeded, batch emulsion copolymerizations of acrylic acid (AA)/styrene and methacrylic acid (MAA)/styrene systems. Data is presented in the form of mass of monomer reacted versus time and conversion of monomer (individual and overall) versus time. The validity of the data is checked by comparing overall conversion/time curves obtained from gravimetric analysis and gas chromatography. Copolymer compositions obtained from the experimental data are shown as a function of overall conversion. The reaction rates of a MAA/styrene copolymerization in which 'cleaned' and 'uncleaned' monomers were utilized are presented. The same recipe and reaction conditions were used in each run.

This report also includes a brief discussion of reactivity ratios for the MAA/styrene and AA/styrene systems. Initial results for particle size measurements are also presented. Partition data presented in the previous progress report (period 6/87 through 11/87) for acid monomer which was neutralized between 0 and 100% with NaOH is reexamined in order to determine whether the acid monomer in both the organic and the acid phases is neutralized to the same extent. Finally, a possible approach for modelling emulsion copolymerization reactions at a degree of neutralization $(DN) > 0$ is discussed.

Kinetic Data

The standard recipe for each of the seeded emulsion copolymerization reactions is given below:

K ₂ S ₂ O ₈	5.0 mMoles/L _{aq}
Sodium Dodecyl Sulfate (SDS)	4.0 mMoles/L _{aq}
	(CMC = 9.0 mMoles/L _{aq})
Seed (particle diameter ~ 27 nm)	~ 30 grams of solid polymer
	(~ 3.05 x 10 ¹⁸ particles/L _{aq})
Monomer	200 grams total
(Acid/Styrene Ratios)	(20/180, 40/160, 70/130)
DI Water	Balance to give 1000 grams total

All reactions were run at 85°C in a nitrogen purged, agitated, 1.0 L glass vessel. The stirrer consisted of a 2-bladed paddle agitator operated at about 600 RPM.

The following procedure was used in each run. Carboxylated, styrene seed latex was mixed for 24 to 48 hours with an anionic/cationic ion exchange resin (Bio-Rex MSZ 501) in order to remove excess surfactant. The amount of surfactant removed from the seed was determined gravimetrically. De-ionized water, 'cleaned' seed, and SDS (an amount which combined with the SDS remaining on the seed gave a concentration of 4.0 mMoles/L_{aq}) was added to the reactor. Nitrogen was bubbled into the reactor and heating via internal stainless steel heating coils was begun. When the reactor temperature reached approximately 85°C, styrene was slowly added through a dropping funnel. The acid monomer was then added in the same manner. Fast addition of either monomer would tend to "shock" the seed resulting in coagulation. The nitrogen purge line was pulled to the level of the

solution after the monomer addition to prevent polymer from coagulating at the interface of the nitrogen bubbles. The system was allowed to equilibrate for 1 to 2 minutes, and a sample was taken to make sure that thermal polymerization had not occurred. The relatively short equilibration time was utilized in order to minimize the risk of thermal polymerization occurring before addition of the initiator. 20 to 25 mL samples were extracted with a syringe every 0.5 to 2.0 minutes for about 10 to 16 minutes. The samples were immediately injected into a chilled hydroquinone solution and immersed in an ice bath to quench the reaction. The reaction mixture was post-reacted for about 30 minutes after the last sample was taken. The overall conversion was measured by drying about 5 grams of each sample overnight in an oven and performing a mass balance on the dried solids.

Individual monomer conversions were obtained by gas chromatography (GC) using a Varian 3300. 5.0 mL portions of the reaction samples were diluted with a mixture of SDS solution, 'uncleaned' seed, and an internal standard solution. The SDS solution and seed were added to help disperse the styrene homogeneously throughout the GC samples. Styrene is essentially insoluble (0.5 g/L) in water. The internal standards consisted of amyl alcohol for the MAA/styrene system and ethylene glycol for the AA/styrene system. Two to four injections per sample were made. The average area ratio of area monomer/area internal standard were obtained for different known monomer concentrations and used to form a calibration curve. This calibration curve was then used to determine monomer concentrations in each of the reaction samples.

Figures 1, 2, 3, 4, 5, and 6 reveal the mass reaction rates of MAA/styrene and AA/styrene copolymerizations at acid monomer weight ratios of 20/180, 40/160, and 70/130. The bold, horizontal lines on each graph represent, from bottom to

top, the amount of acid monomer, styrene monomer, and total monomer fed to the reactor. The same data is plotted in Figures 7, 8, 9, 10, 11, and 12 in the form of individual and overall monomer conversion versus time.

The seeded reactions required only 10 to 20 minutes to reach high conversion. Unseeded homopolymerization reactions of styrene often require several hours to reach high conversion. The use of the seed causes the reaction to occur much more quickly. These reaction rates with the acids are slightly faster than the reaction rate of a seeded styrene homopolymerization as shown by experimental data in Figure 13 and by simulation in Figure 14. (The simulation calculations used constants which reflected the actual operating conditions used in the reaction. A value for the propagation constant of styrene at 85°, $k_p=900$ L/mole s, was obtained from the literature. The number of particles, $N_p=3.05E18$, was based on the amount of seed used. The amount of swelling of the particles (volume of monomer in particles/volume of polymer in particles ≈ 1.5) was based on work with styrene polymerizations performed by Jansson [3]. The average number of radicals per particle was varied from 0.1 to 0.3. A value of $\bar{n}=0.25$ gives a good fit to the experimental data.) The slight increase in rate when acid monomer is present is expected due to the higher propagation constants of these acids (16,000 L/mole s, MAA; 100,000 - 250,000 L/mole s, AA) relative to styrene (900 L/mole s).

MAA reacts more quickly than does AA despite the fact that its propagation constant is less than that of AA. The reason for its faster rate is attributed to the fact that it is more hydrophobic than AA so that it distributes to a greater extent inside the particles where the monomer concentrations are higher than in the aqueous phase. MAA reaches high conversion at about the same time as styrene. However, for the same ratios of acid/styrene, the AA conversion significantly lags that of

STYMAA10 MASS REACTION RATES

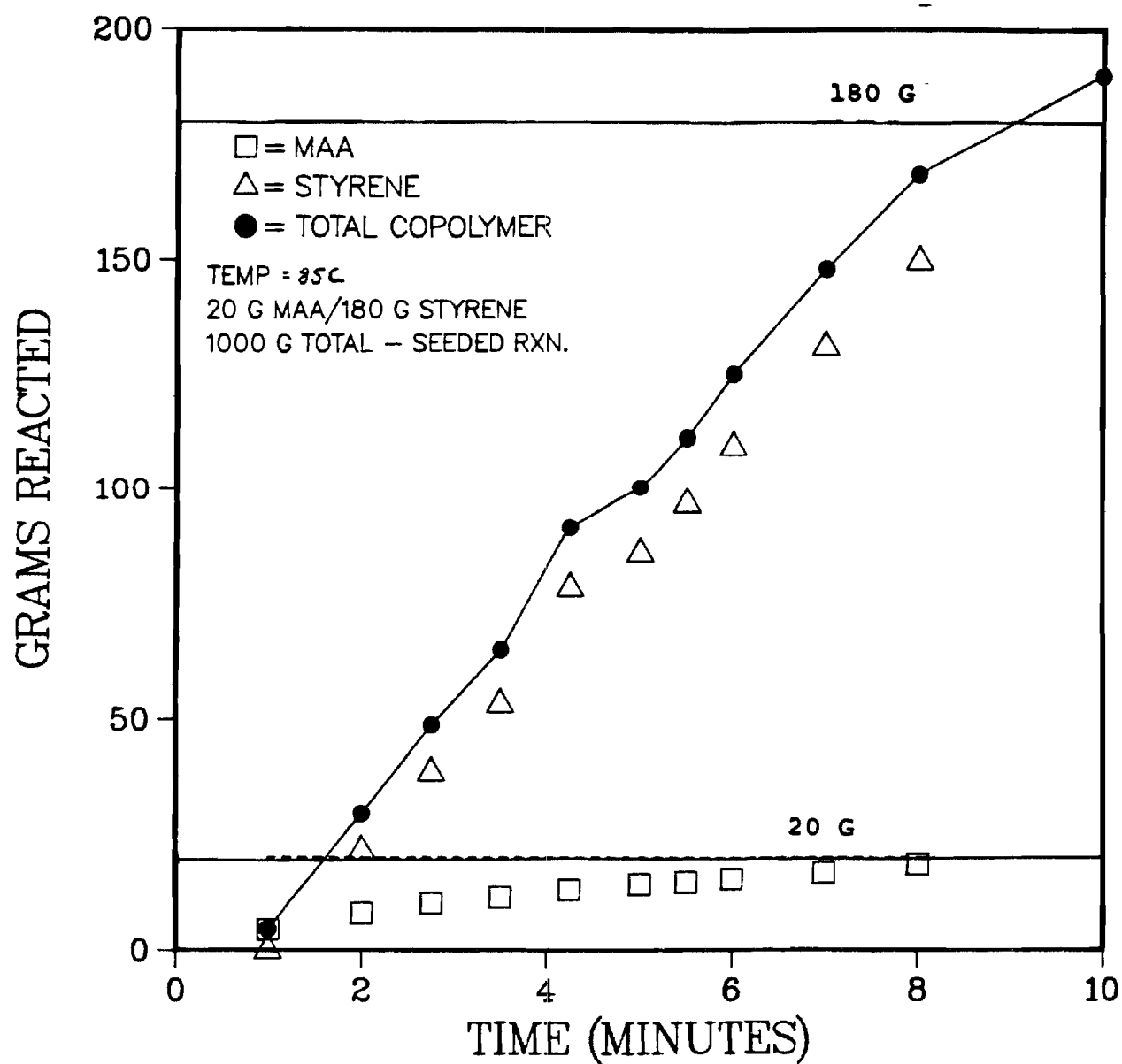


Figure 1: Mass reaction rates for emulsion copolymerization of MAA/styrene in a weight ratio of 20/180.

STY/MAA8 MASS REACTION RATES

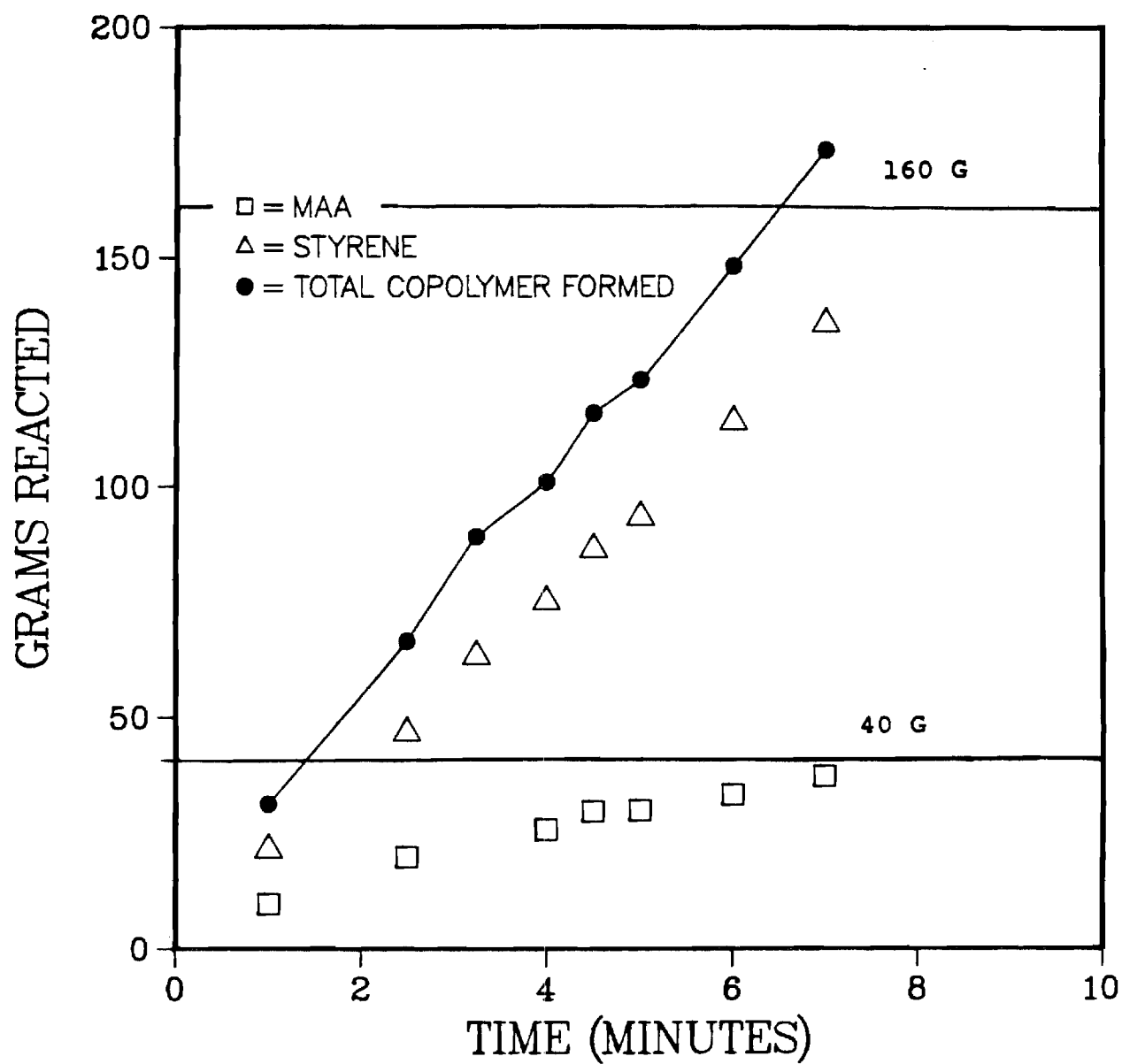


Figure 2: Mass reaction rates for emulsion copolymerization of MAA/styrene in a weight ratio of 40/160.

STYMAA9 MASS REACTION RATES

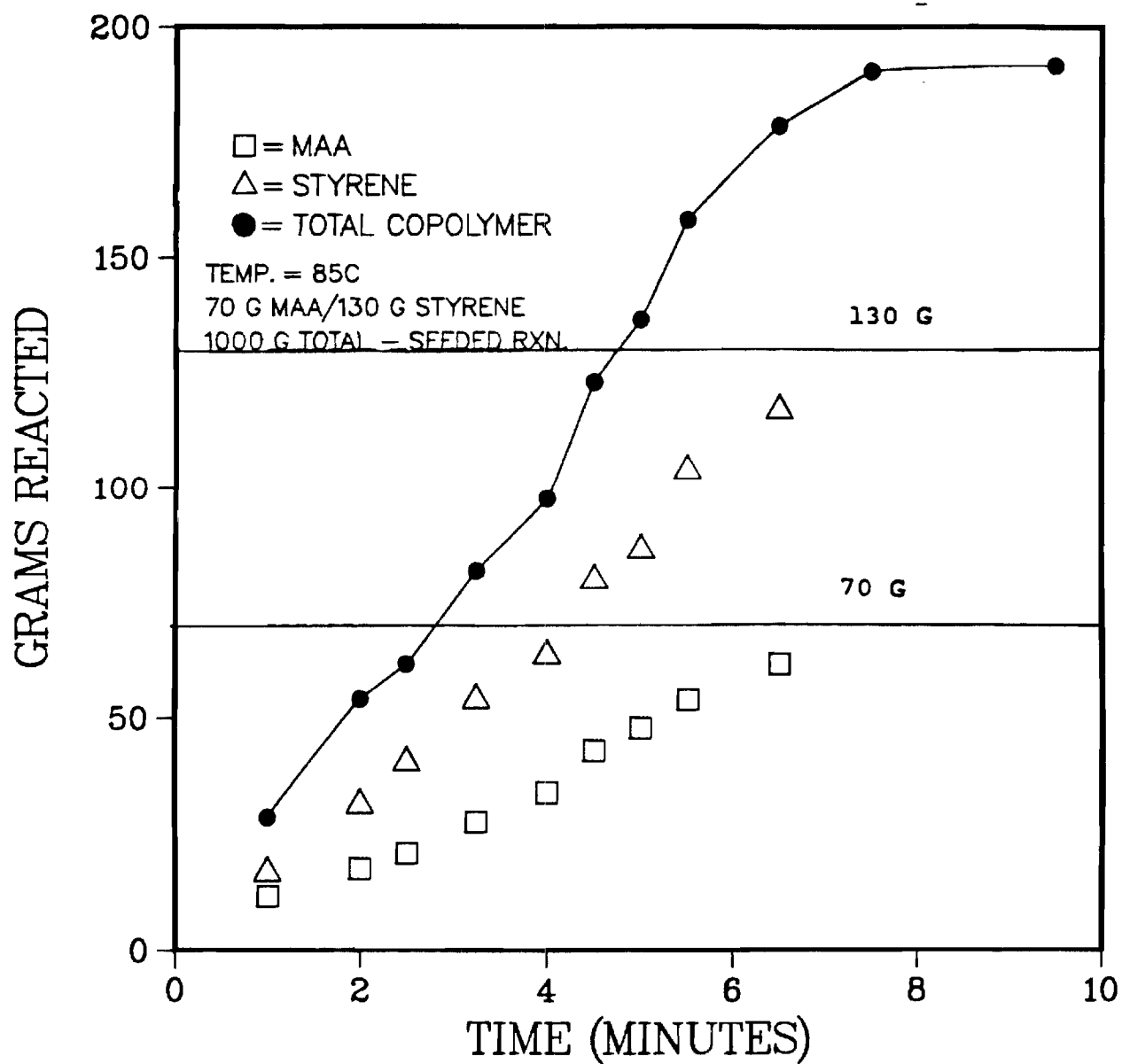


Figure 3: Mass reaction rates for emulsion copolymerization of MAA/styrene in a weight ratio of 70/130.

STYAA8 MASS REACTION RATES

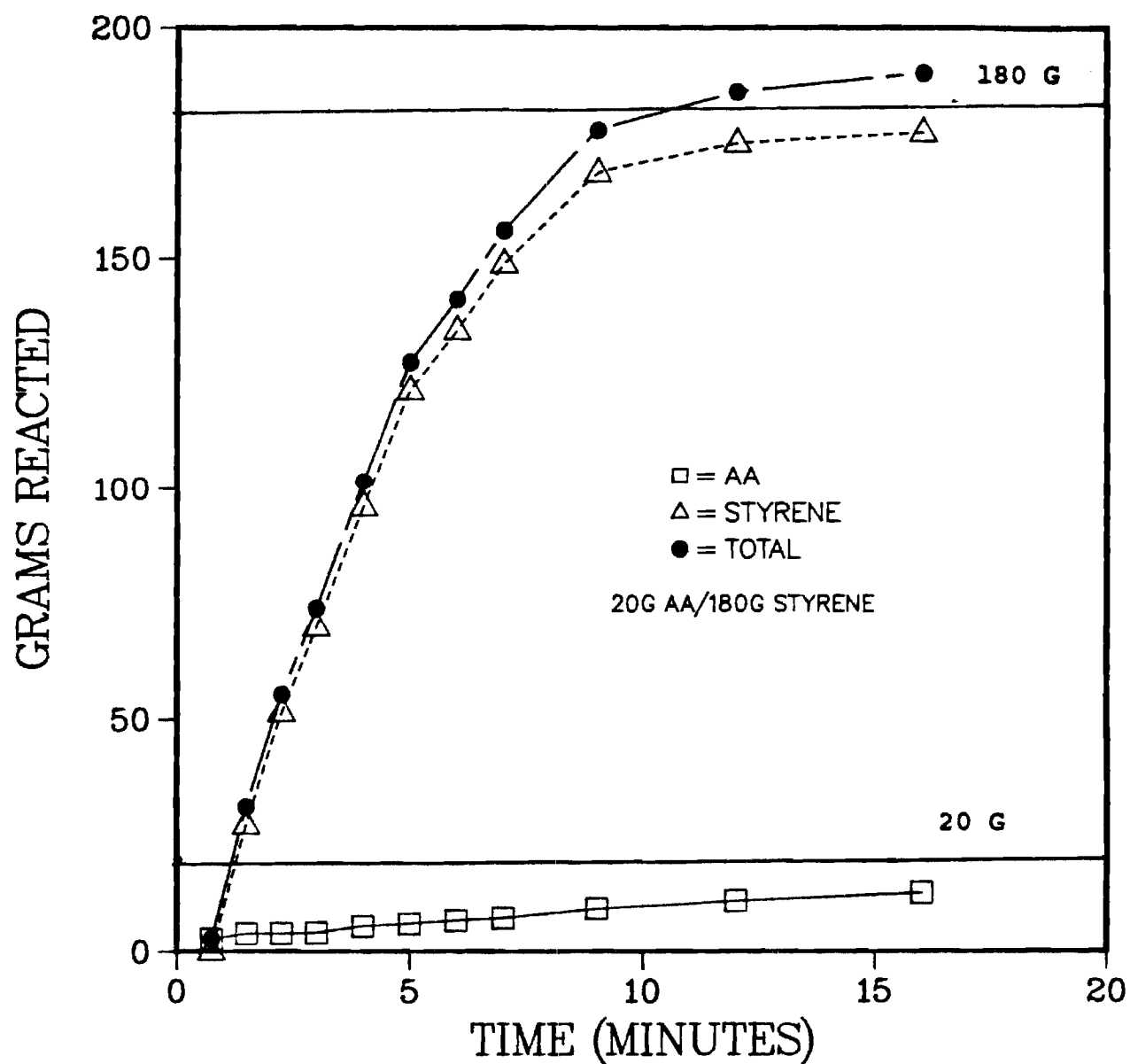


Figure 4: Mass reaction rates for emulsion copolymerization of AA/styrene in a weight ratio of 20/180.

STYAA7 MASS REACTION RATES

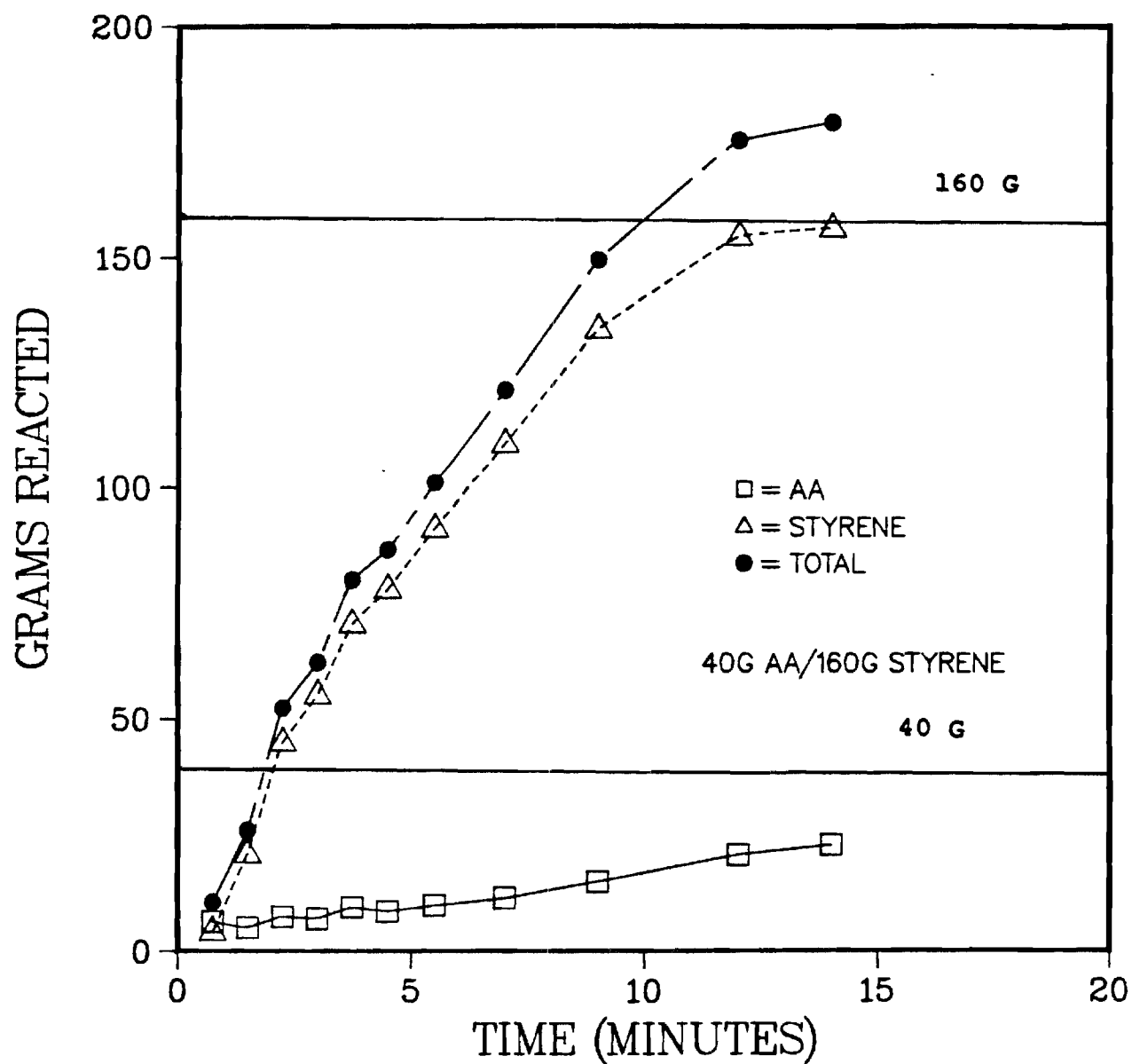


Figure 5: Mass reaction rates for emulsion copolymerization of AA/styrene in a weight ratio of 40/160.

STYAA6 MASS REACTION RATES

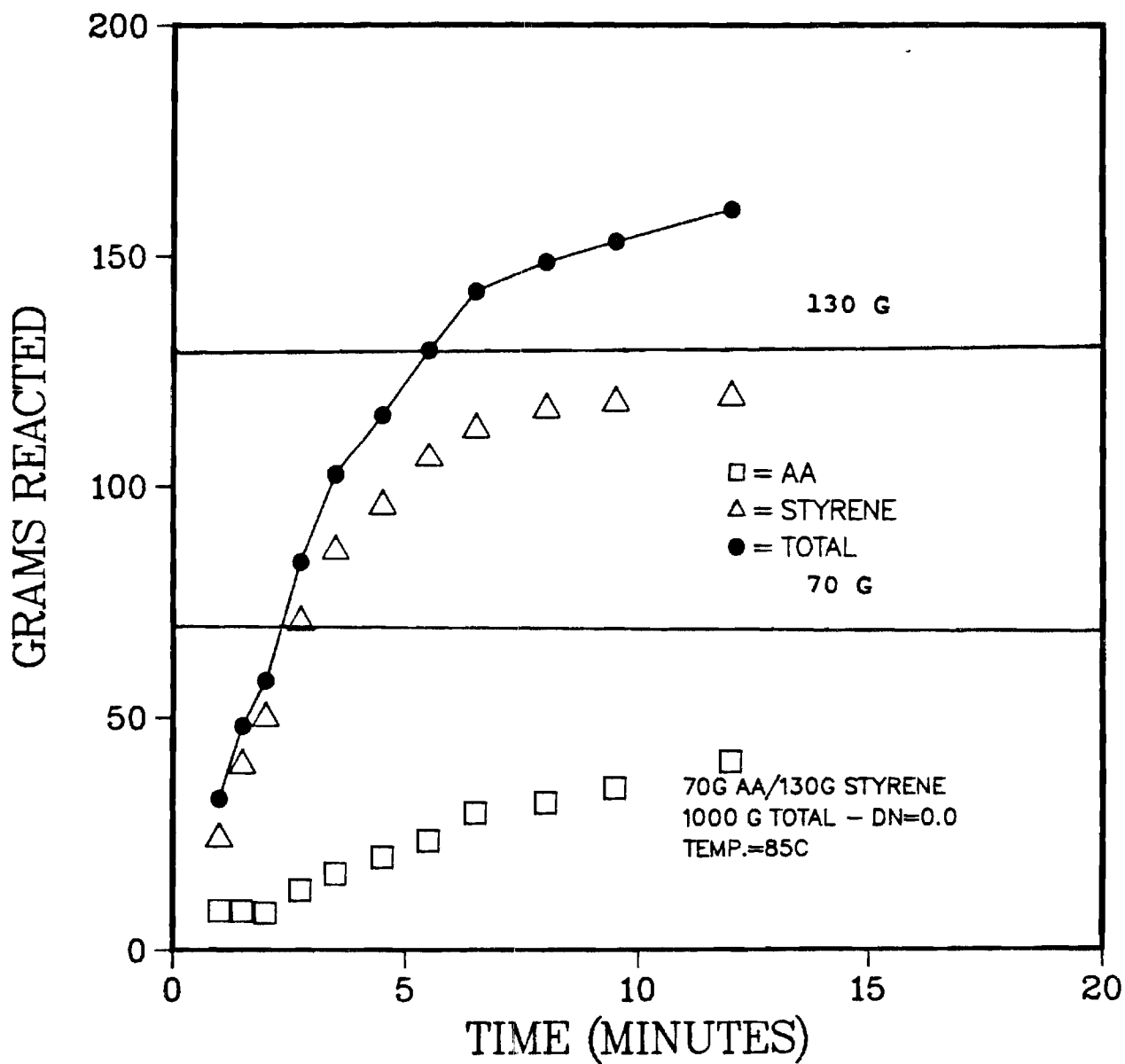


Figure 6: Mass reaction rates for emulsion copolymerization of AA/styrene in a weight ratio of 70/130.

STYMAA10 CONV./TIME DATA

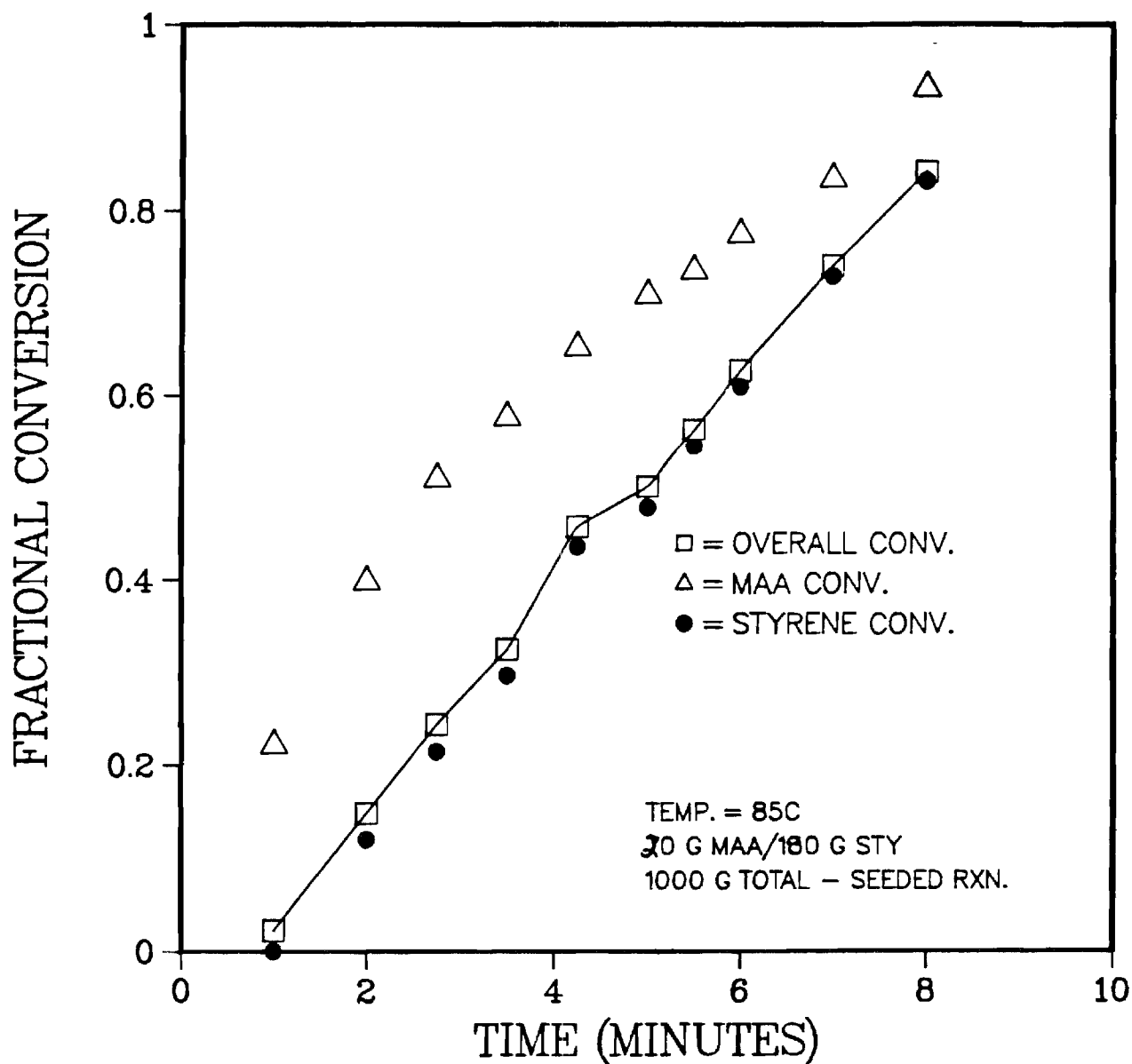


Figure 7: Conversion/time curves for emulsion copolymerization of MAA/styrene in a weight ratio of 20/180.

STY/MAA8 CONV./TIME DATA

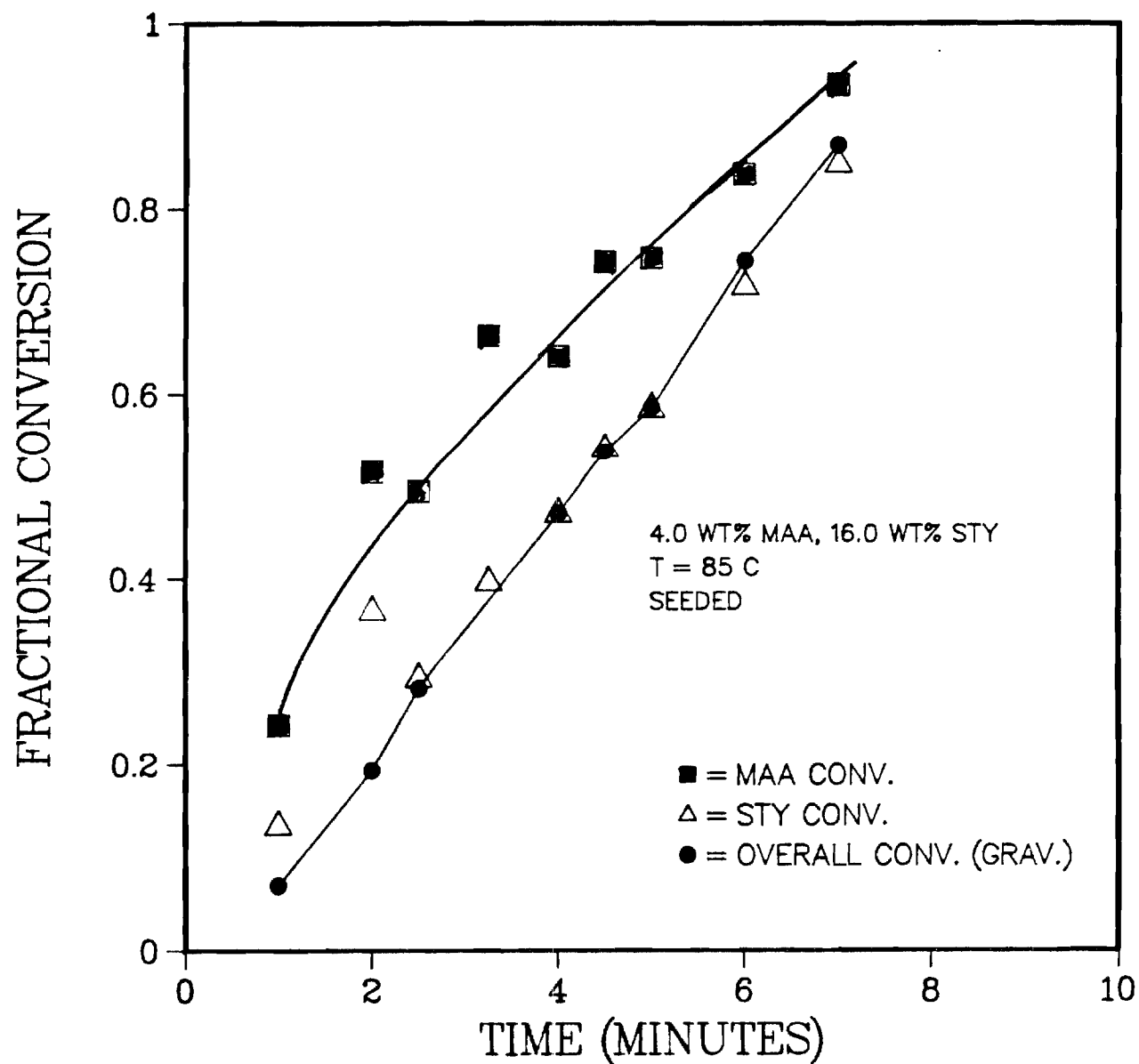


Figure 8: Conversion/time curves for emulsion copolymerization of MAA/styrene in a weight ratio of 40/160.

STYMAA9 CONV./TIME DATA

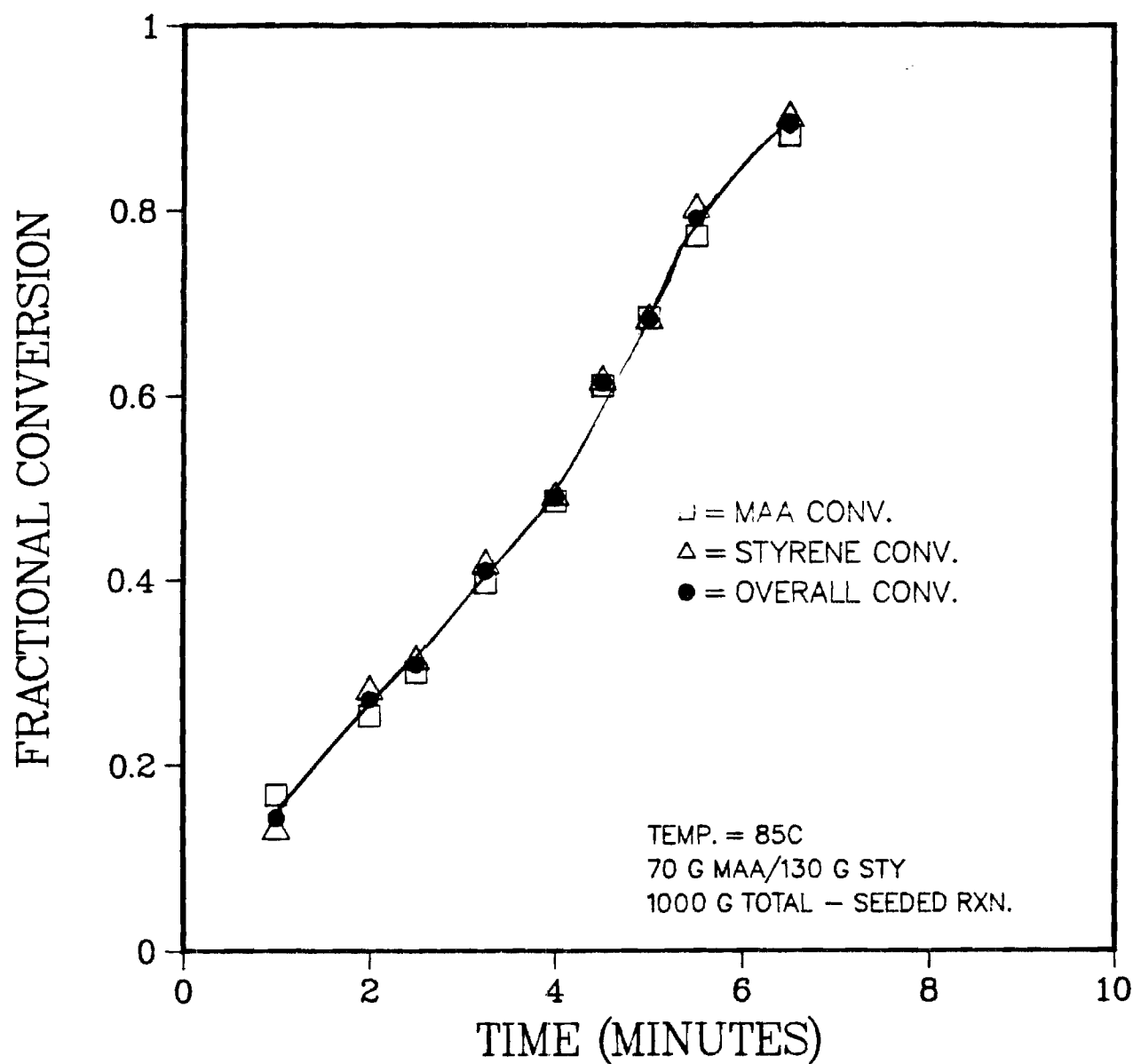


Figure 9: Conversion/time curves for emulsion copolymerization of MAA/styrene in a weight ratio of 70/130.

STYAA8 CONV/TIME DATA

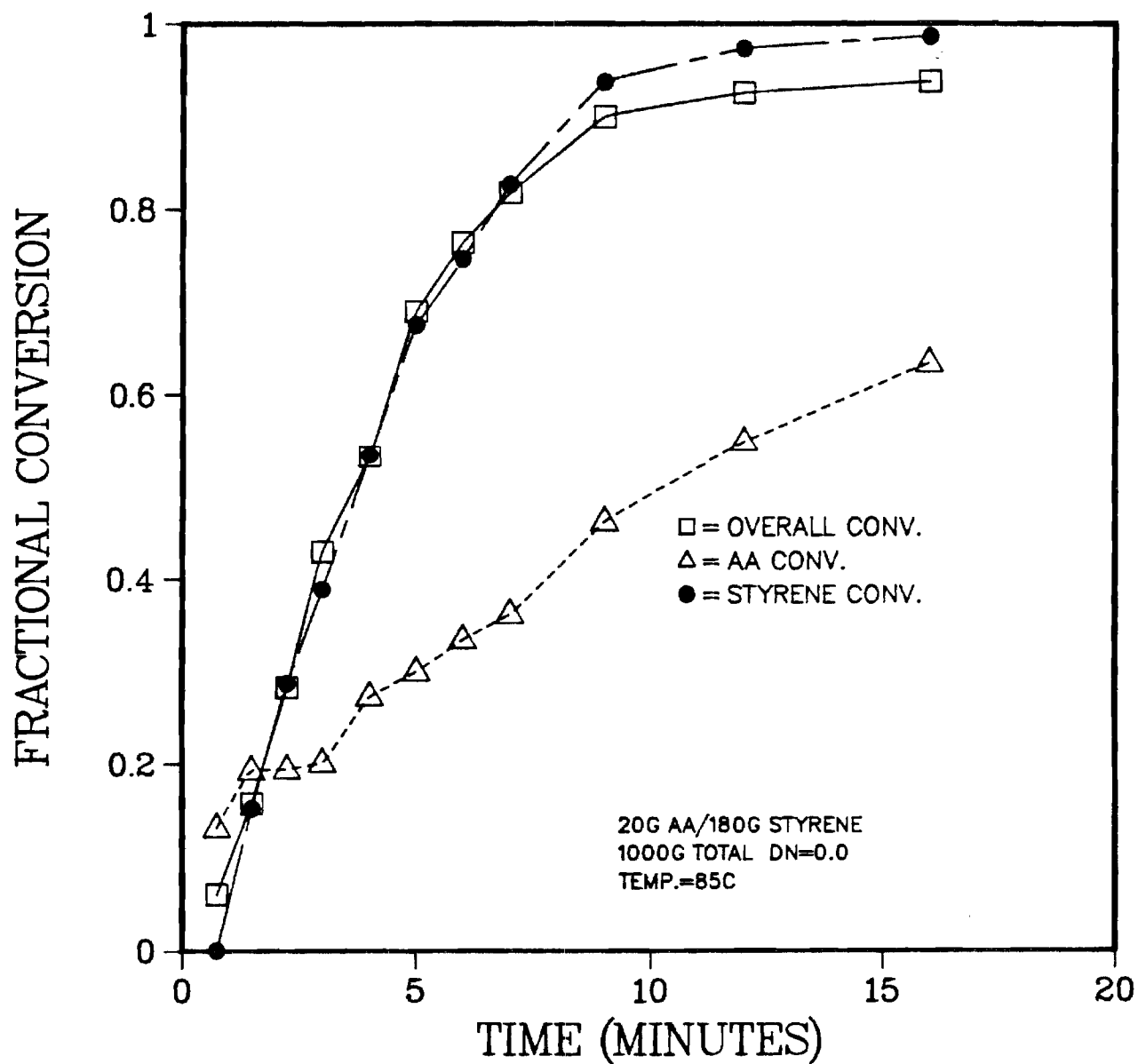


Figure 10: Conversion/time curves for emulsion copolymerization of AA/styrene in a weight ratio of 20/180.

STYAA7 CONV/TIME DATA

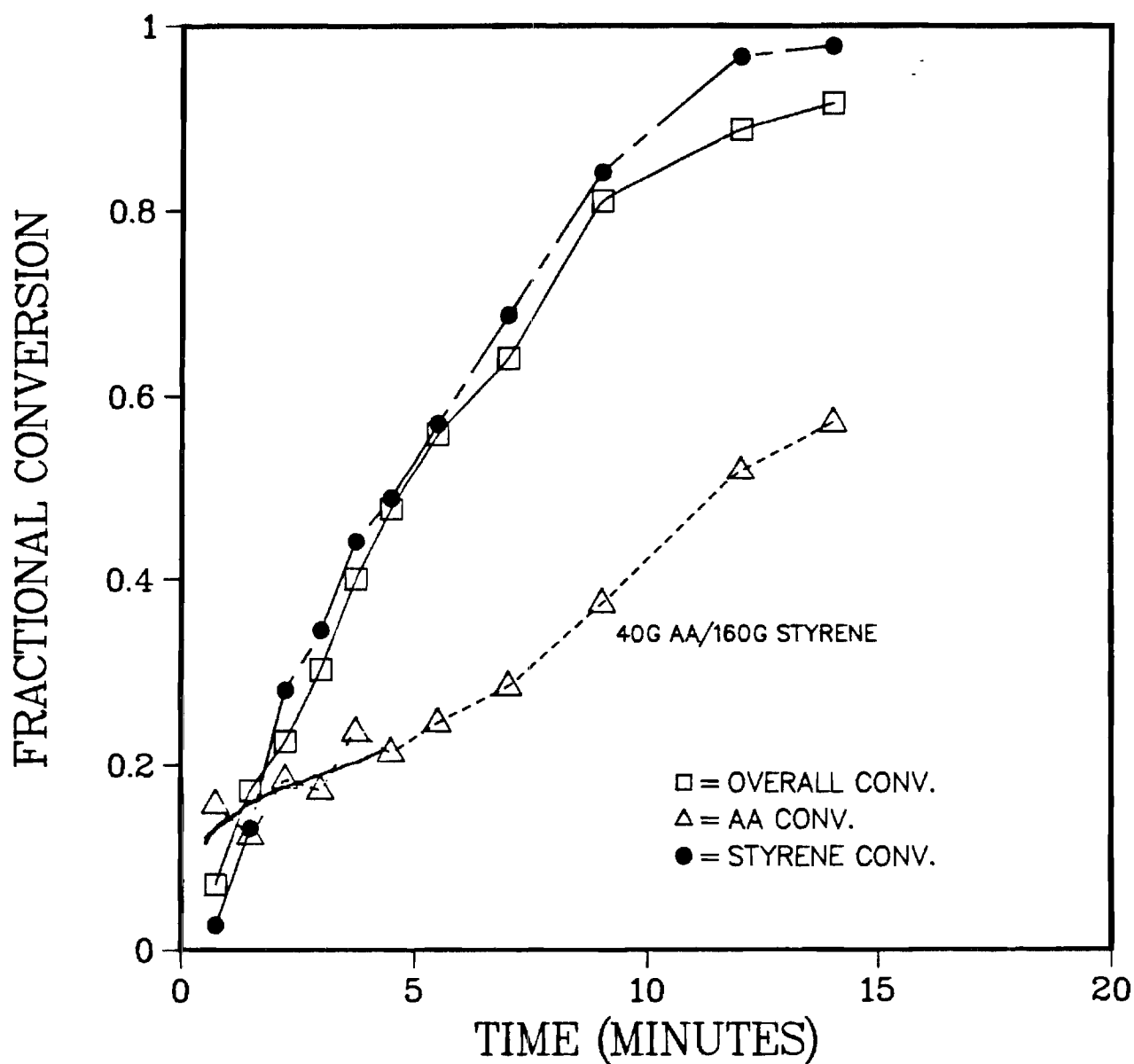


Figure 11: Conversion/time curves for emulsion copolymerization of AA/styrene in a weight ratio of 40/160.

STYAA6 CONVERSION/TIME CURVES

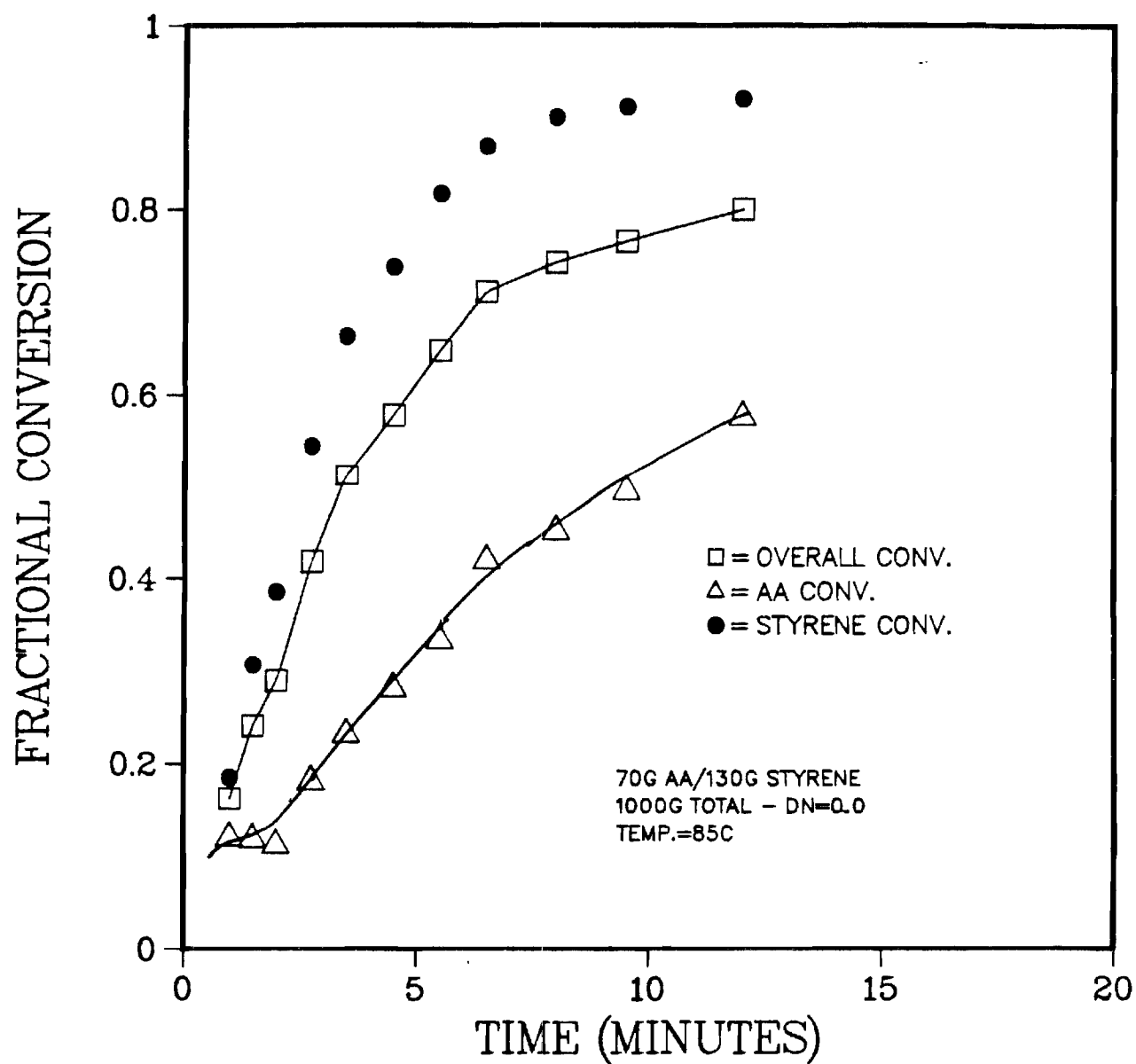


Figure 12: Conversion/time curves for emulsion copolymerization of AA/styrene in a weight ratio of 70/130.

styrene. A substantial portion of AA does not react until after most of the styrene monomer has been depleted. These differences in the AA and MAA reaction rates produce significant differences in the acid/styrene copolymer compositions which will be discussed later.

The conversion-time curves for AA in the three AA/styrene reactions reveal a rather unusual feature. The conversion appears to jump to about 12 to 17% over the first minute. It then tends to level out for about another minute before climbing at a more consistent rate. Some additional data obtained from unseeded reactions run at lower temperatures reveals this same trend.

One explanation for this behavior may be that an equilibration process between acid inside the particles and acid in the aqueous phase may be occurring. The reaction rate initially may be so high in the particles that it exceeds the rate at which acid from the aqueous phase diffuses into the particles to resupply the main reaction site. MAA, which diffuses more easily into the particles than AA, does not exhibit this behavior. Very simple mass transfer calculations, however, reveal that diffusion into such small particles is normally very fast. Therefore, unless the diffusion coefficients for AA into the particles are greatly reduced due to the solid polymer comprising the particles, or additional resistances due to surfactant and/or polymer at the particle interface impede the ability of the AA monomer to enter the particle, this reasoning may not be valid.

A better explanation may be that the initial reaction occurs in the aqueous phase since partition experiments suggest that about 90% of the AA is present in this phase at the start of the reaction. Very little styrene reacts over the first minute, but about 15 to 20% of the AA reacts over this period. The primary reaction site may then transfer to the particles as the oligomeric radicals in the aqueous phase

HOMOSTY1 SEEDED HOMOPOLYMERIZATION OF STYRENE

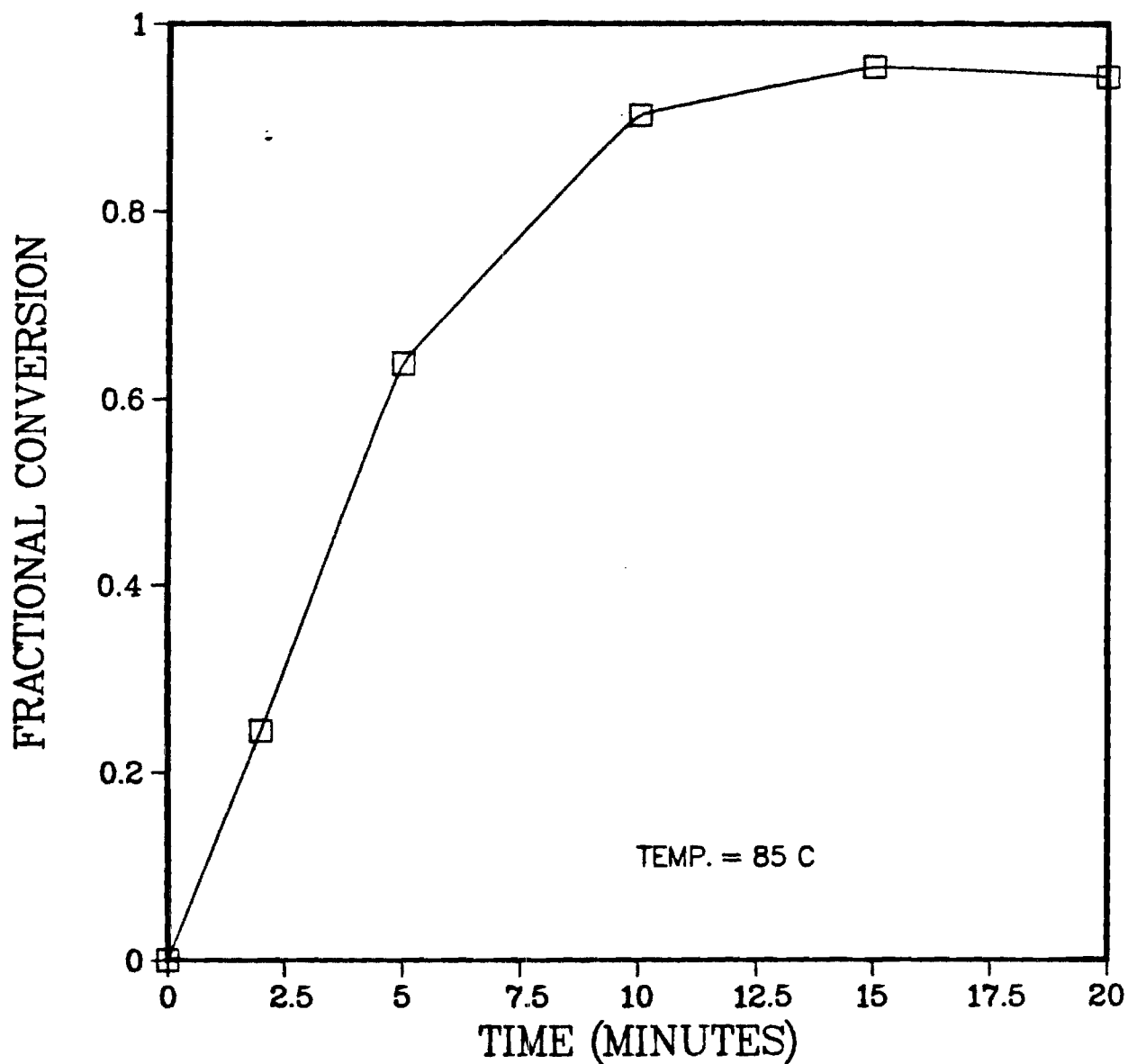


Figure 13: Rate of reaction of seeded homopolymerization of styrene. The recipe and reaction conditions were identical to those used in the acid/styrene copolymerizations except that no acid was used in the reaction.

SIMULATED SEEDED HOMOPOLY. RATE OF STYRENE

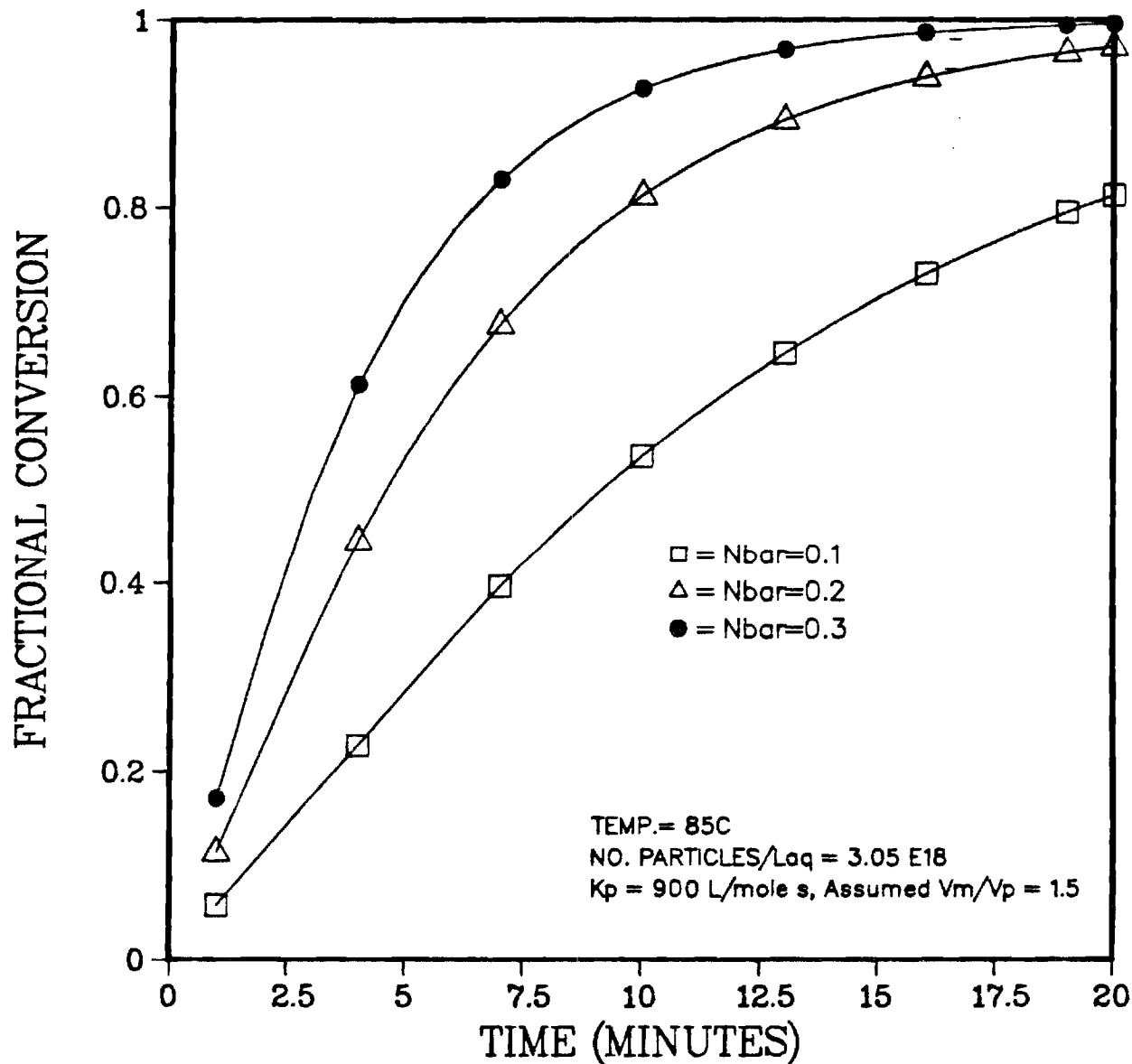


Figure 14: Simulated results for the rate of reaction of seeded homopolymerization of styrene. The recipe and reaction conditions assumed were identical to those used in the acid/styrene copolymerizations except that no acid was used in the reaction.

become large enough and hydrophobic enough (due to a small portion of styrene monomer which is available for reaction in the aqueous phase) to become irreversibly attracted to the particles. Reactions with MAA do not result in this 'plateau' in the conversion/time curve. However, the amount of MAA in the aqueous phase is much less than that of AA due to its more hydrophobic nature. Only about 50% of the MAA is present in the aqueous phase at the start of the reaction based on initial partition experiments.

Another point to consider is that the homopolymerization reaction of AA is not a simple free-radical addition reaction as discussed in the previous report. AA monomer may complex with itself and with linear AA polymer chains along which the propagation may quickly 'zip'. This complicated reaction mechanism may contribute to the unusual behavior observed in the copolymer system. Further investigation into these phenomena will continue.

Test for Reliability of the Conversion Data

Initial work with the gas chromatograph proved to be very trying. Gross inconsistencies in the overall conversion obtained from gravimetry and GC analysis caused initial data to be very unreliable. Inhomogeneous mixtures of the unreacted styrene contributed to some of these problems. Various improvements in sample preparation procedures and operation of the gas chromatograph were explored until these inconsistencies were eliminated. Conversion data is deemed to be reliable when overall conversions obtained from gravimetry and gas chromatography agreed within $\pm 5\%$. Plots of overall conversion versus time obtained by these two methods for the previous six reactions are shown in Figures 15, 16, 17, 18, 19, and 20.

Except for some inconsistency at high conversion in run STY/AA-6, the agreement between the two methods appears to be very good.

Copolymer Composition

Compositions for the copolymer formed in each of the six reactions were calculated from the experimental data using bulk reaction assumptions. (These calculations will need to be modified once more partition data is obtained.) The data were replotted as mass of monomer *i* reacted versus overall conversion and fitted by a third order polynomial via regression analysis to give an equation of the following form:

$$\text{Mass Monomer } i \text{ Reacted} = A + BX + CX^2 + DX^3 \quad (1)$$

where *X* = overall fractional conversion. The equations were then used to obtain overall monomer concentrations over the conversion period. The change in monomer concentrations over small increments of conversion were then calculated and used to determine both the instantaneous and cumulative copolymer compositions. The results for all six runs are shown in Figures 21, 22, 23, 24, 25, and 26. Extrapolation of the regression equations beyond the point at which overall conversions were measured (> 85 to 90%) produced cumulative copolymer compositions which did not exactly match the feed compositions in some cases. This discrepancy was most noticeable in the AA/styrene runs because as much as 40% of the acid reacted during the last 10% of the overall conversion period. Since data during this last portion of the overall reaction was not taken, the fitted regression equations could not predict the sharp change in the shape of the mass AA versus overall fractional conversion

STYMAA10 GRAVIMETRIC VS. GC_CONV.

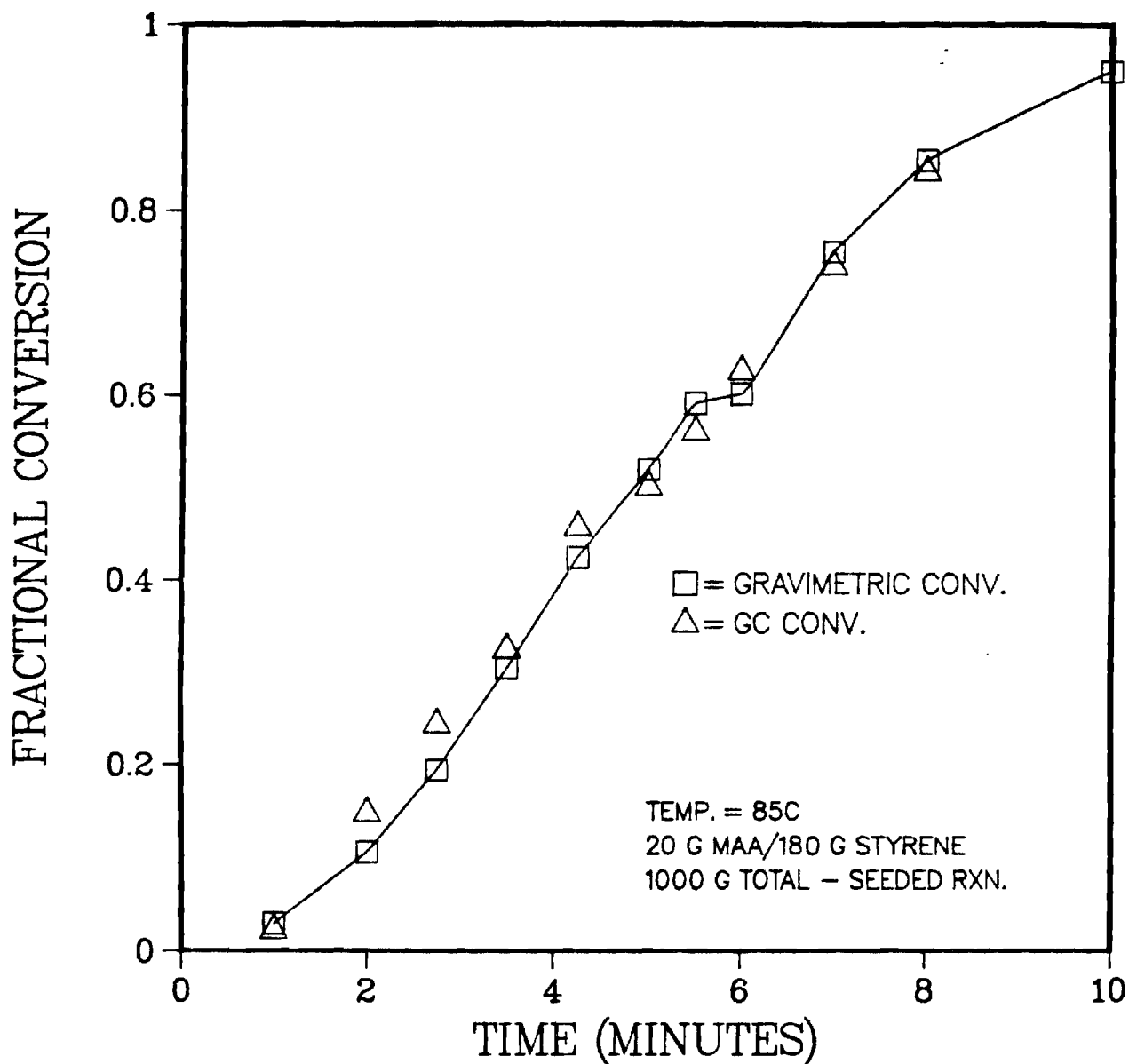


Figure 15: Comparison of overall conversion obtained from gravimetry and gas chromatography for emulsion copolymerization of MAA/styrene at a weight ratio of 20/180.

STY/MAA8 GC VS. GRAV. CONV. MEASUREMENTS

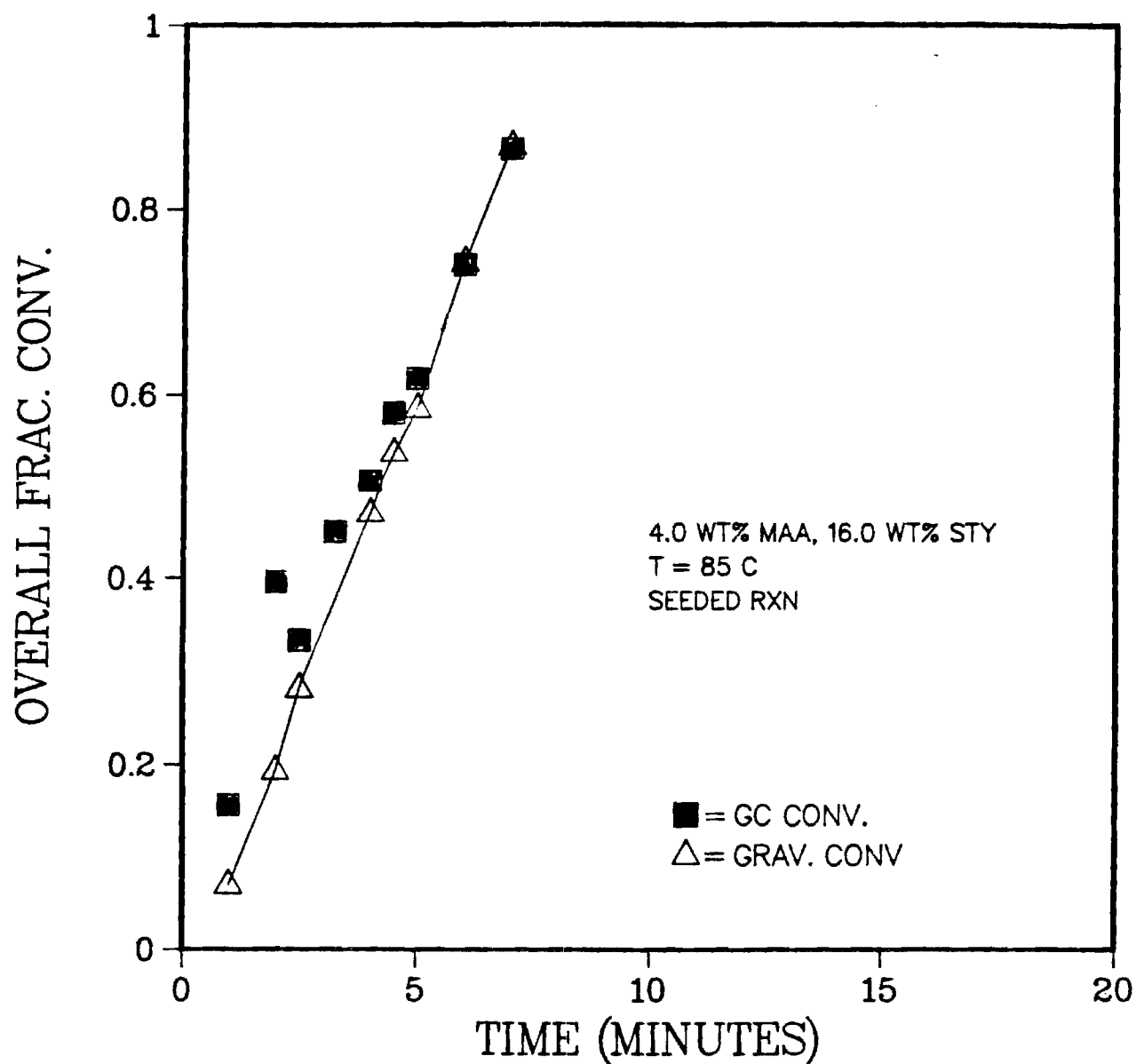


Figure 16: Comparison of overall conversion obtained from gravimetry and gas chromatography for emulsion copolymerization of MAA/styrene at a weight ratio of 40/160.

STYMAA9 GRAVIMETRIC VS. GC OVERALL CONV.

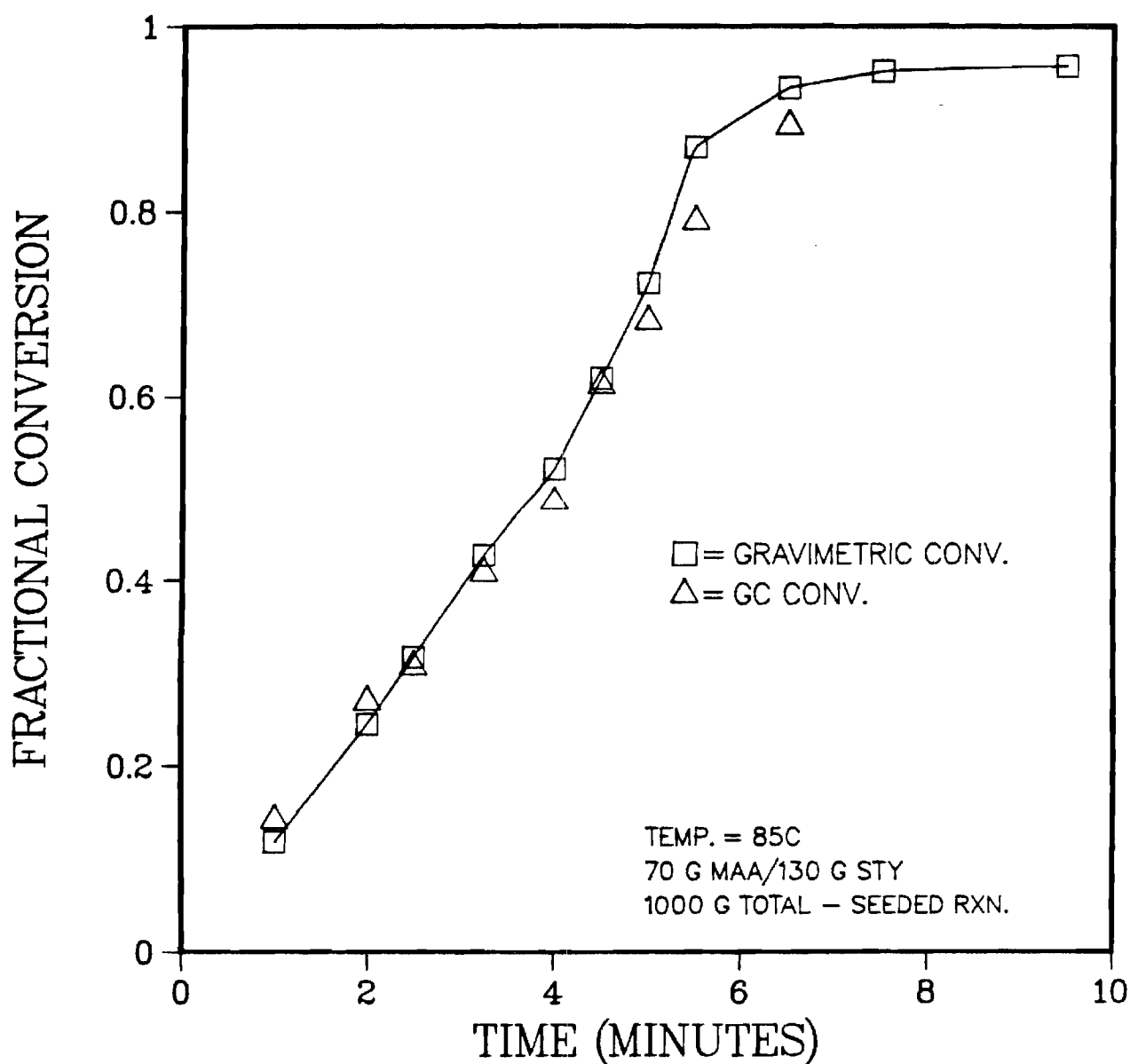


Figure 17: Comparison of overall conversion obtained from gravimetry and gas chromatography for emulsion copolymerization of MAA/styrene at a weight ratio of 70/130.

STYAA8 GC AND GRAV. CONVERSIONS

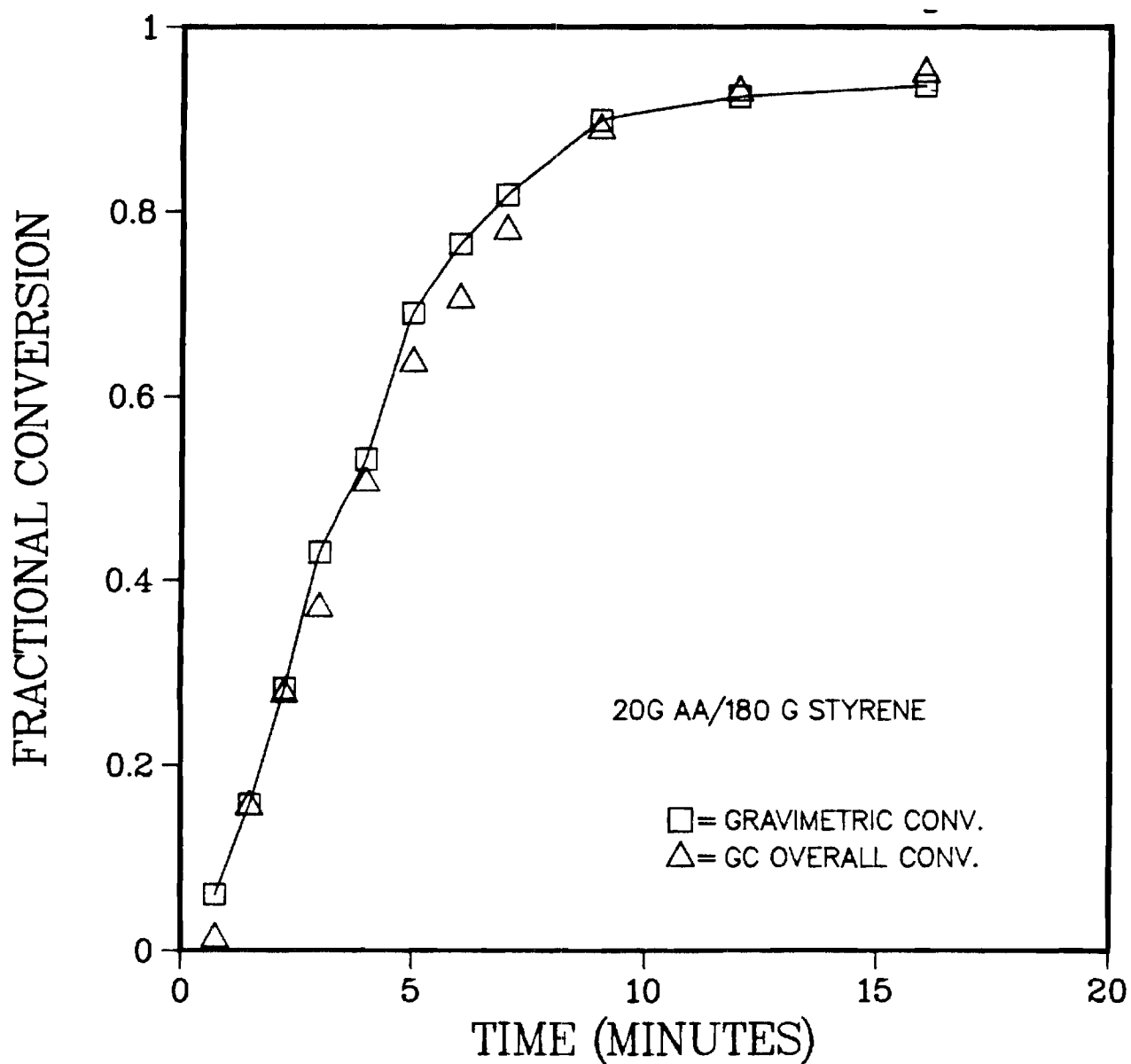


Figure 18: Comparison of overall conversion obtained from gravimetry and gas chromatography for emulsion copolymerization of AA/styrene at a weight ratio of 20/180.

STYAA7 GC AND GRAVIMETRIC CONVERSIONS

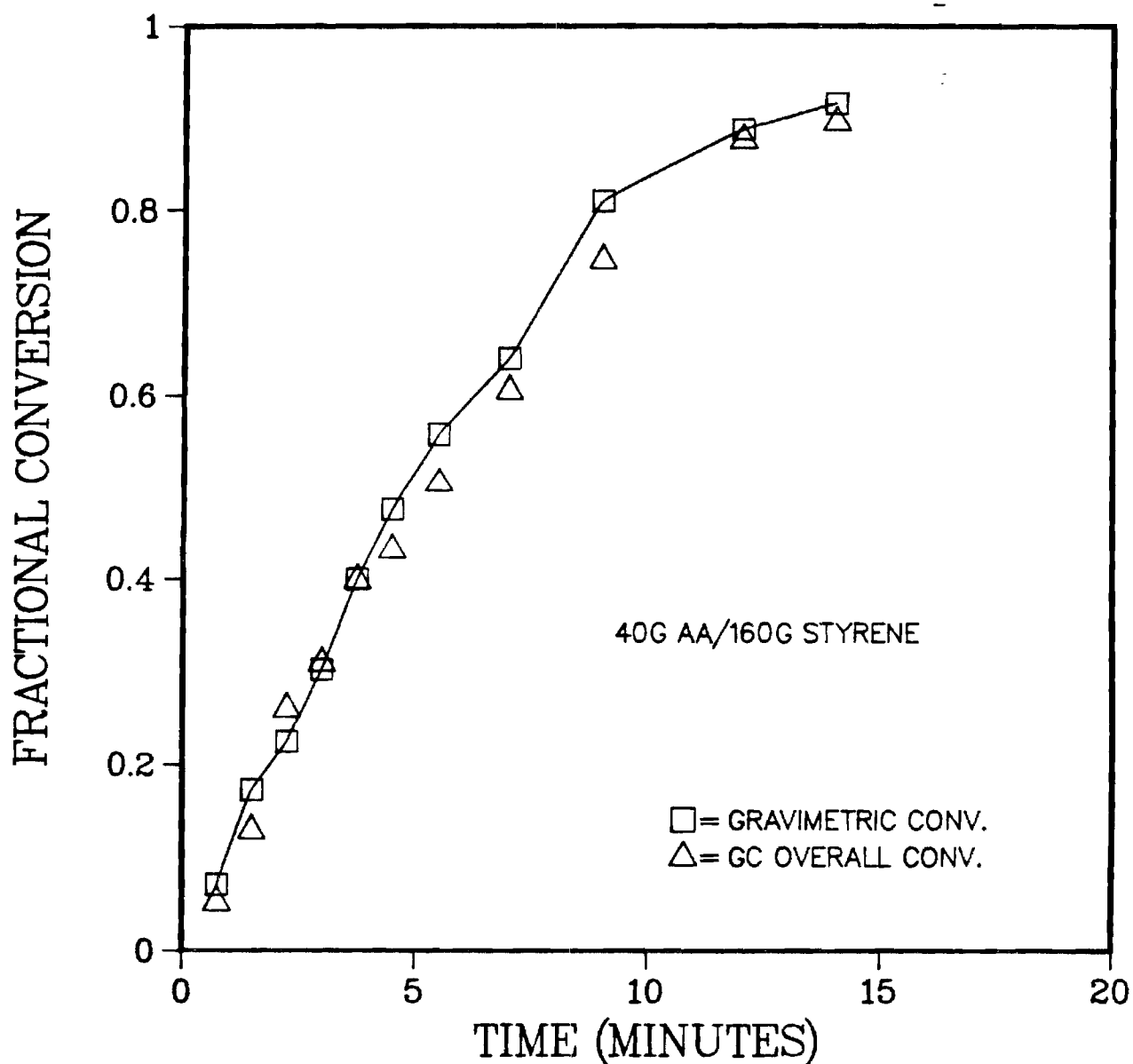


Figure 19: Comparison of overall conversion obtained from gravimetry and gas chromatography for emulsion copolymerization of AA/styrene at a weight ratio of 40/160.

STYAA6 GRAV. AND GC OVERALL CONVERSION CURVES

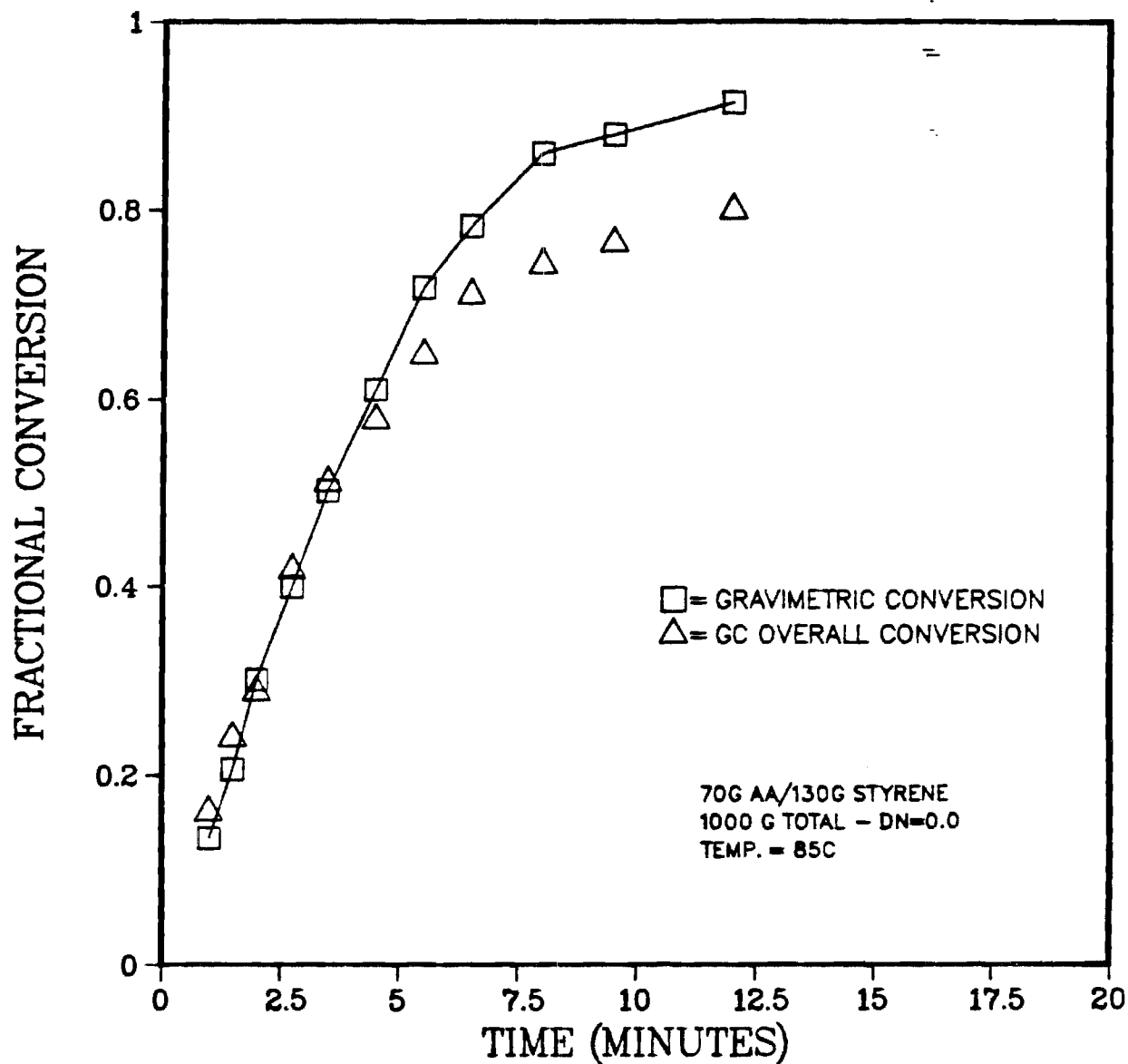


Figure 20: Comparison of overall conversion obtained from gravimetry and gas chromatography for emulsion copolymerization of AA/styrene at a weight ratio of 70/130.

curve over the last 10% overall conversion. Therefore, copolymer composition curves at high conversions were not calculated for these runs. The expected shape of these curves, however, was estimated for high conversions. These estimated values are given by the dashed lines in the previous figures.

Several runs, especially with acrylic acid, revealed a decreasing then increasing trend in the instantaneous copolymer composition curves. This type of behavior may be influenced by the initial plateau in the conversion/time curve for AA. Thus a possible non-equilibrium situation may have a significant influence, not only on the kinetics, but also on the initial copolymer compositions.

Reactivity Ratios

Calculation of reactivity ratios in an emulsion system should account for the partition of the monomers between the particle and aqueous phases. However, since detailed partition data is not yet at hand, initial calculations of reactivity ratios using the Mayo-Lewis approach for bulk or solution systems were performed. Several points were taken from each of the runs at the three different monomer ratios and used to calculate R_1 versus R_2 (reactivity ratios for styrene and acid, respectively) lines via the Mayo-Lewis method. Each pair of points from a single run should produce the same R_1 versus R_2 line. Variation between the lines obtained from pairs of monomer conversion values did exist in some cases. Therefore, an 'average' line was used for each of the three runs and plotted in Figure 27 for the MAA/styrene system. The point of intersection of the lines from the three different runs identifies the reactivity ratios. The intersection triangle is supposed to represent the experimental error. Results for the AA/styrene reactions did not

COPOLYMER COMPOSITION STYMAA-10

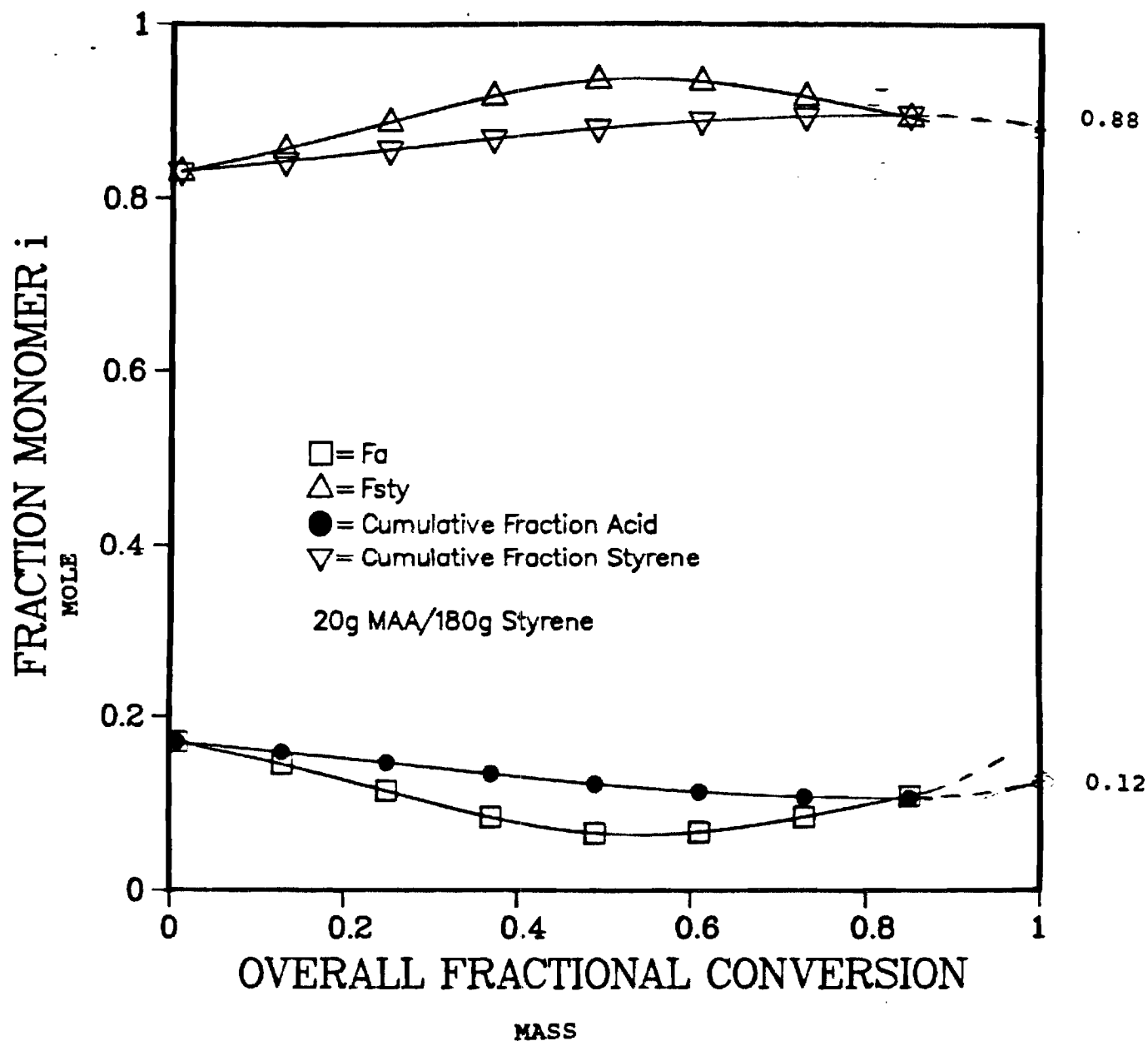


Figure 21: Instantaneous and cumulative copolymer compositions calculated from experimental data from emulsion copolymerization of MAA and styrene in a weight ratio of 20/180. Partition of the monomers was not taken into account in the calculations.

COPOLYMER COMPOSITION STYMAA-8

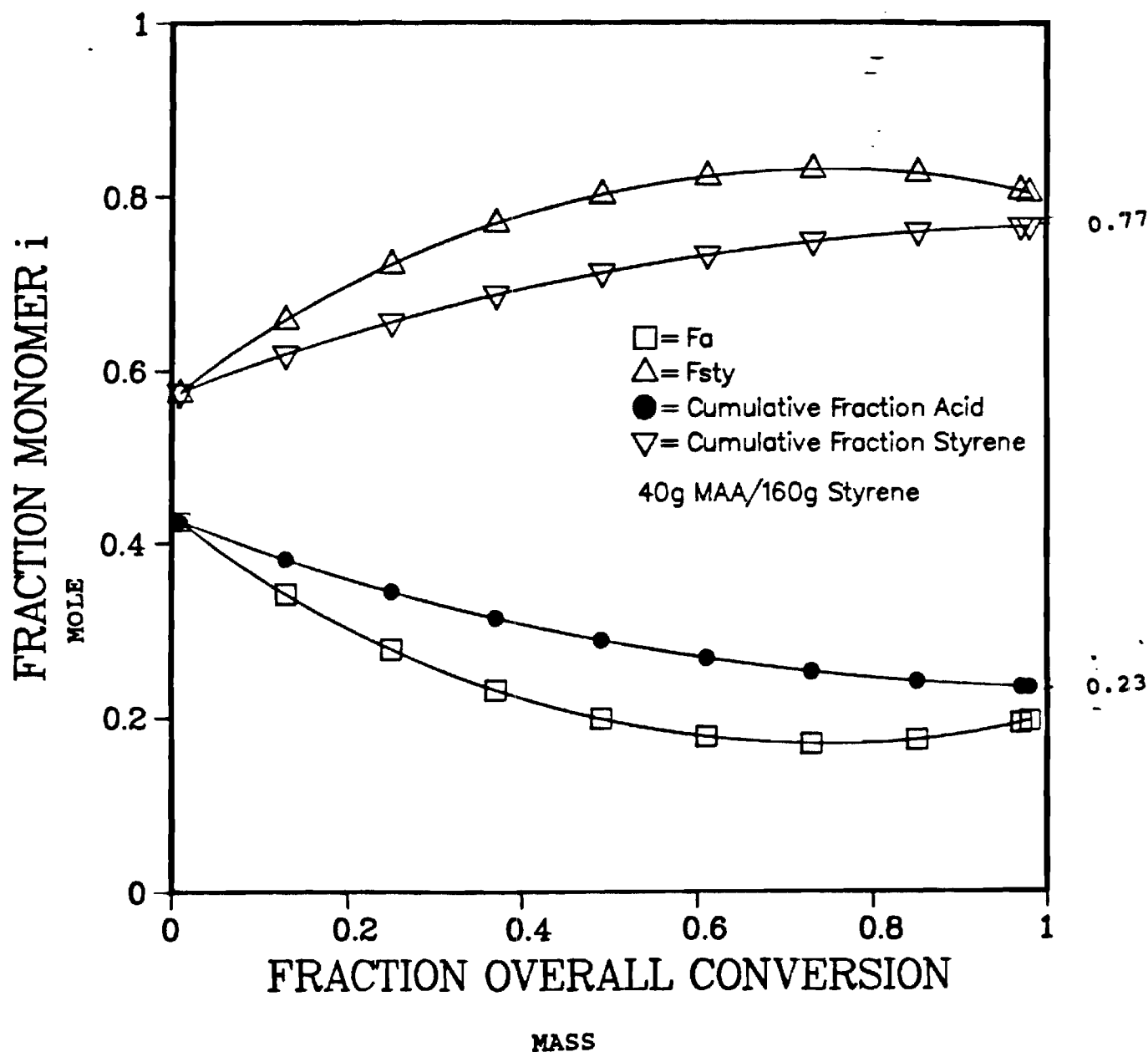


Figure 22: Instantaneous and cumulative copolymer compositions calculated from experimental data from emulsion copolymerization of MAA and styrene in a weight ratio of 40/160. Partition of the monomers was not taken into account in the calculations.

COPOLYMER COMPOSITION

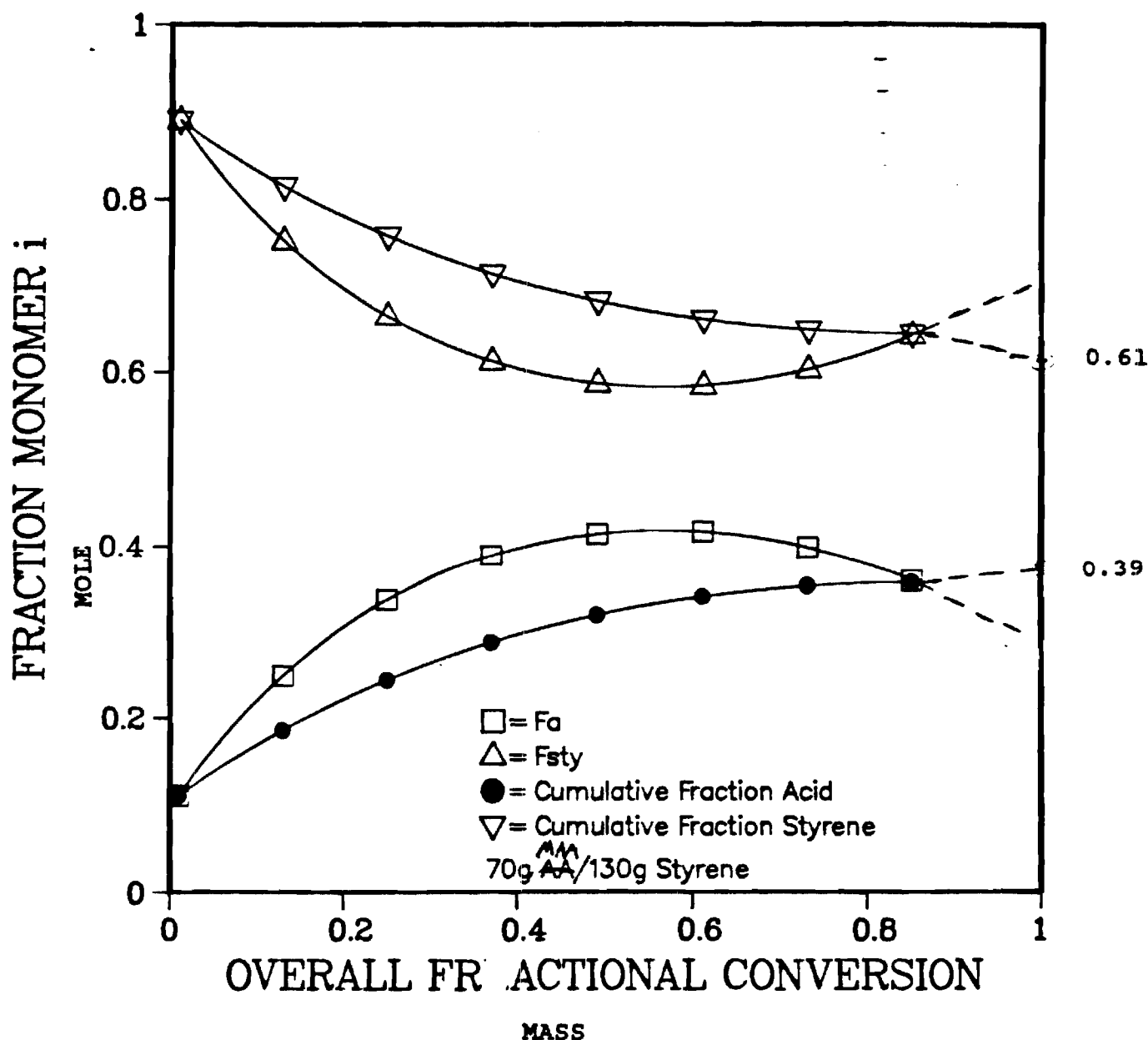


Figure 23: Instantaneous and cumulative copolymer compositions calculated from experimental data from emulsion copolymerization of MAA and styrene in a weight ratio of 70/130. Partition of the monomers was not taken into account in the calculations.

COPOLYMER COMPOSITION STYAA-8

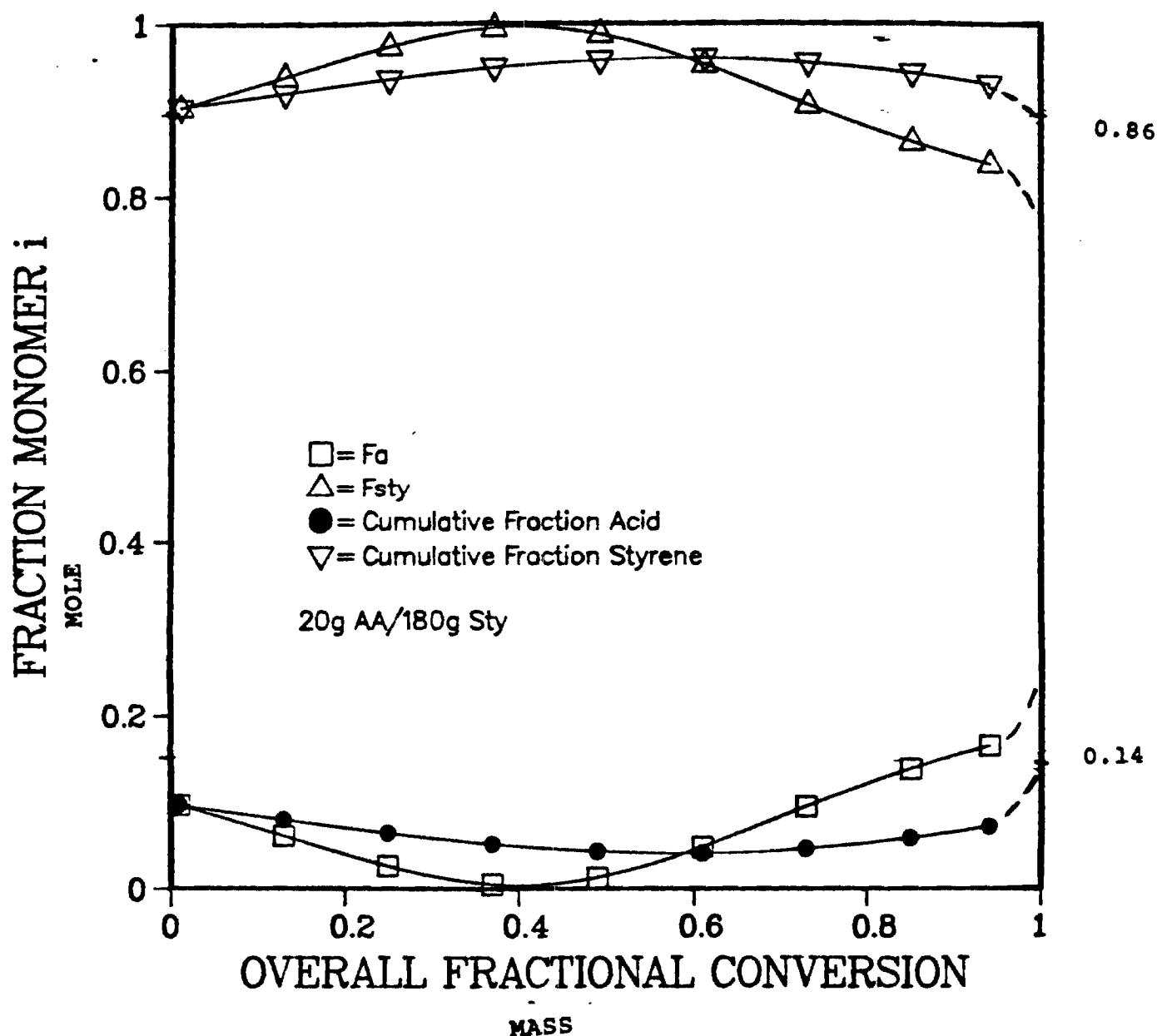


Figure 24: Instantaneous and cumulative copolymer compositions calculated from experimental data from emulsion copolymerization of AA and styrene in a weight ratio of 20/180. Partition of the monomers was not taken into account in the calculations.

COPOLYMER COMPOSITION STYAA-7

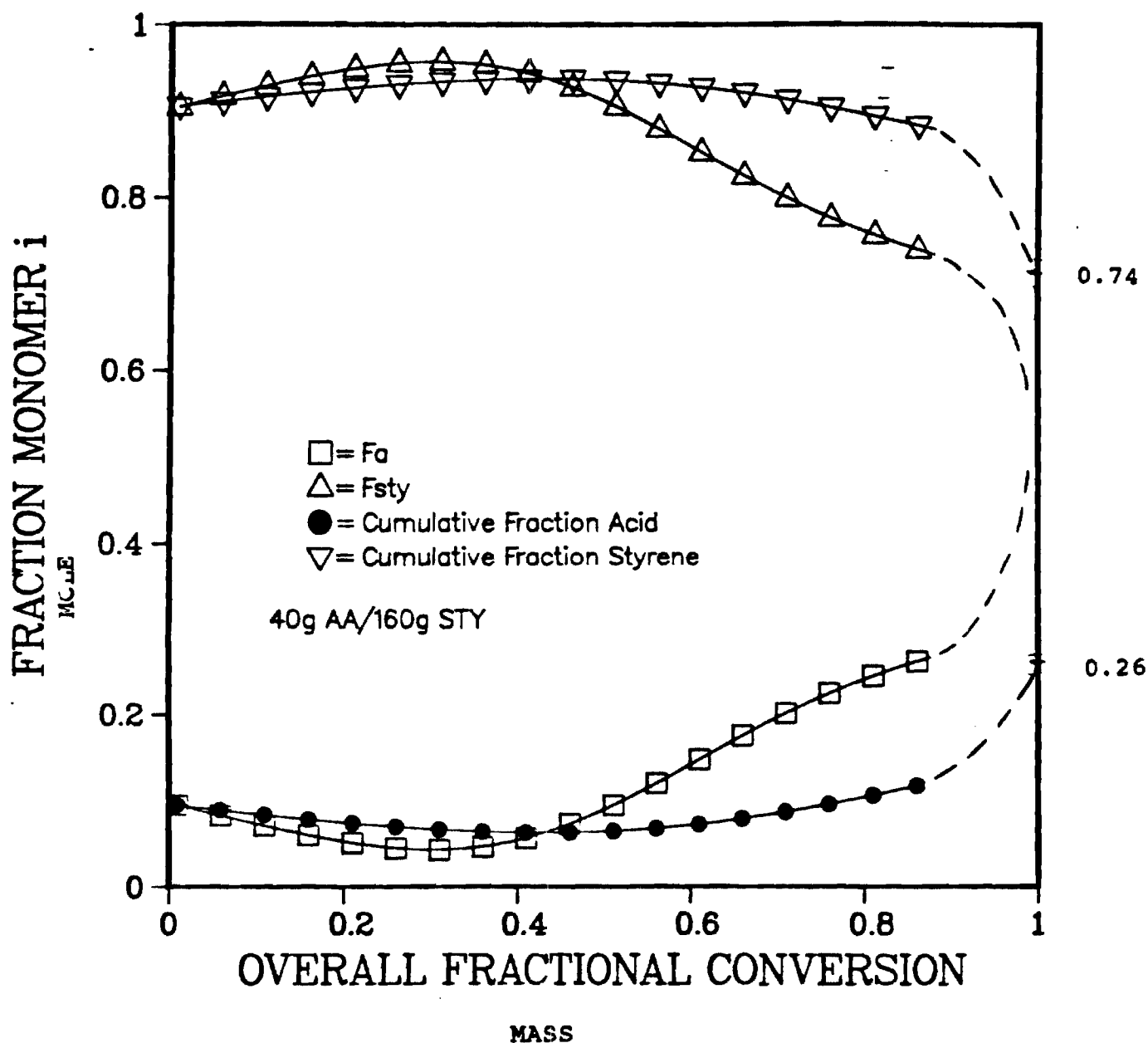


Figure 25: Instantaneous and cumulative copolymer compositions calculated from experimental data from emulsion copolymerization of AA and styrene in a weight ratio of 40/160. Partition of the monomers was not taken into account in the calculations.

COPOLYMER COMPOSITION

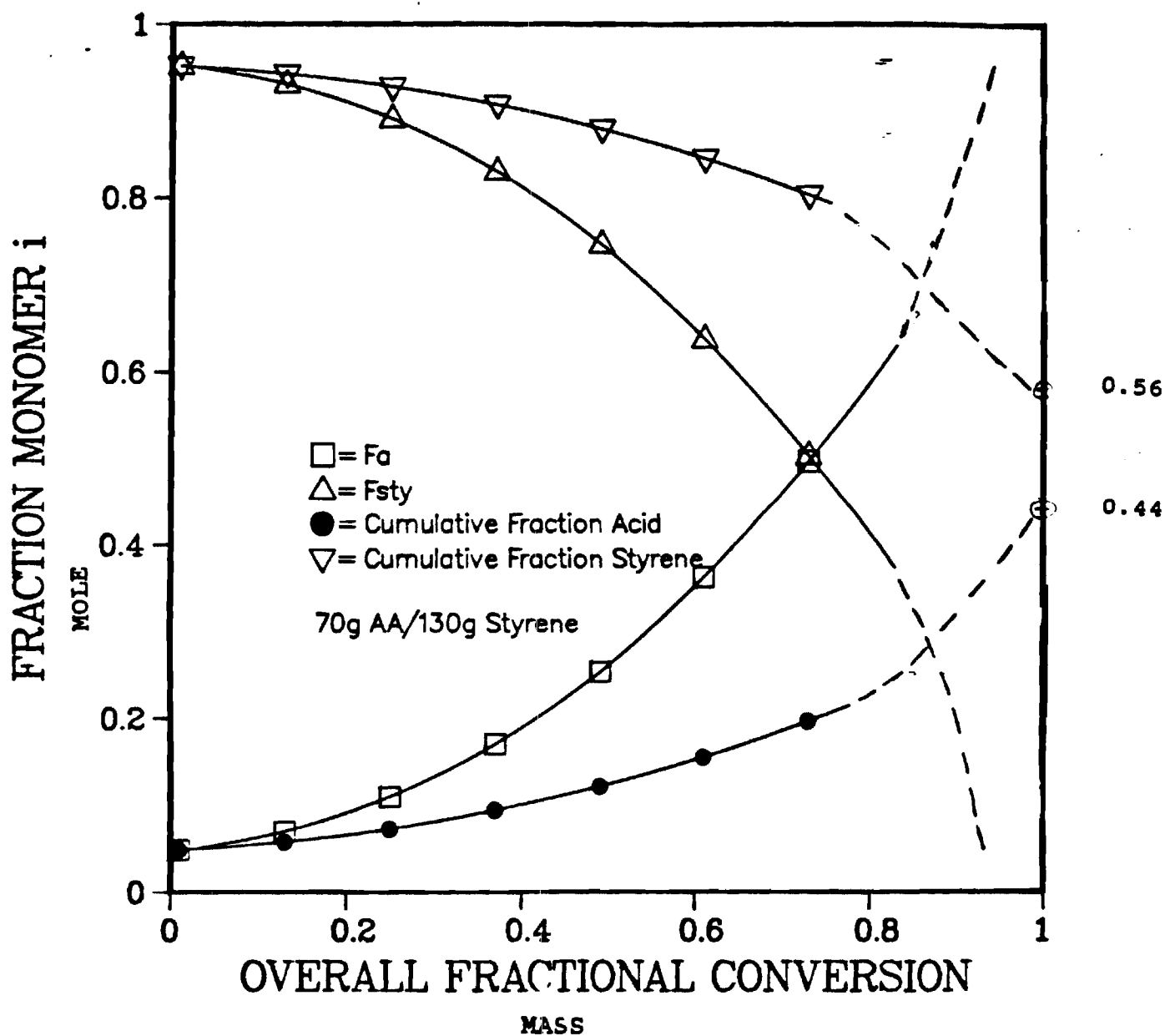


Figure 26: Instantaneous and cumulative copolymer compositions calculated from experimental data from emulsion copolymerization of AA and styrene in a weight ratio of 70/130. Partition of the monomers was not taken into account in the calculations.

produce reasonable results. The exclusion of partition information may have contributed to the problems in calculating reactivity ratios for the AA/styrene system. Nevertheless, better methods are needed to calculate reactivity ratios for emulsion reaction systems involving carboxylic acids. These methods should account for the partitioning of the monomers for emulsion systems as discussed by Schuller [1].

Reaction Rates of Cleaned and Uncleaned Monomers

All of the reactions discussed to this point employed monomers which contained a small amount of inhibitor added by the manufacturer to prevent polymerization during shipping. It is usually necessary to remove all traces of inhibitor when performing continuous polymerizations since inhibitor is continuously being added to the reactor in the feed. Removal of inhibitor is not normally necessary in most batch runs since the only effect in most cases is the occurrence of an induction period at the initial stage of the reaction during which the inhibitor is consumed. The reaction then proceeds in normal fashion. Such an induction period was not noticed in any of the previous runs. The high temperature (85°C) may have contributed in masking any such induction period. Nevertheless, a MAA/styrene run (STY/MAA-11) was repeated using 'cleaned' monomers in order to compare the reaction rate to that obtained from using 'uncleaned' monomers. Styrene was washed with NaOH then filtered through an alumina packing. The MAA was distilled under vacuum.

The conversion time results are plotted alongside a run (STY/MAA- 8) performed with 'uncleaned' monomers. (See Figure 28.) The nearly identical conversion/time data suggests that any effect of the inhibitors in the monomers is negligible when run under these reaction conditions. A similar run is planned for the AA/styrene system.

MAYO-LEWIS MAA/STYRENE

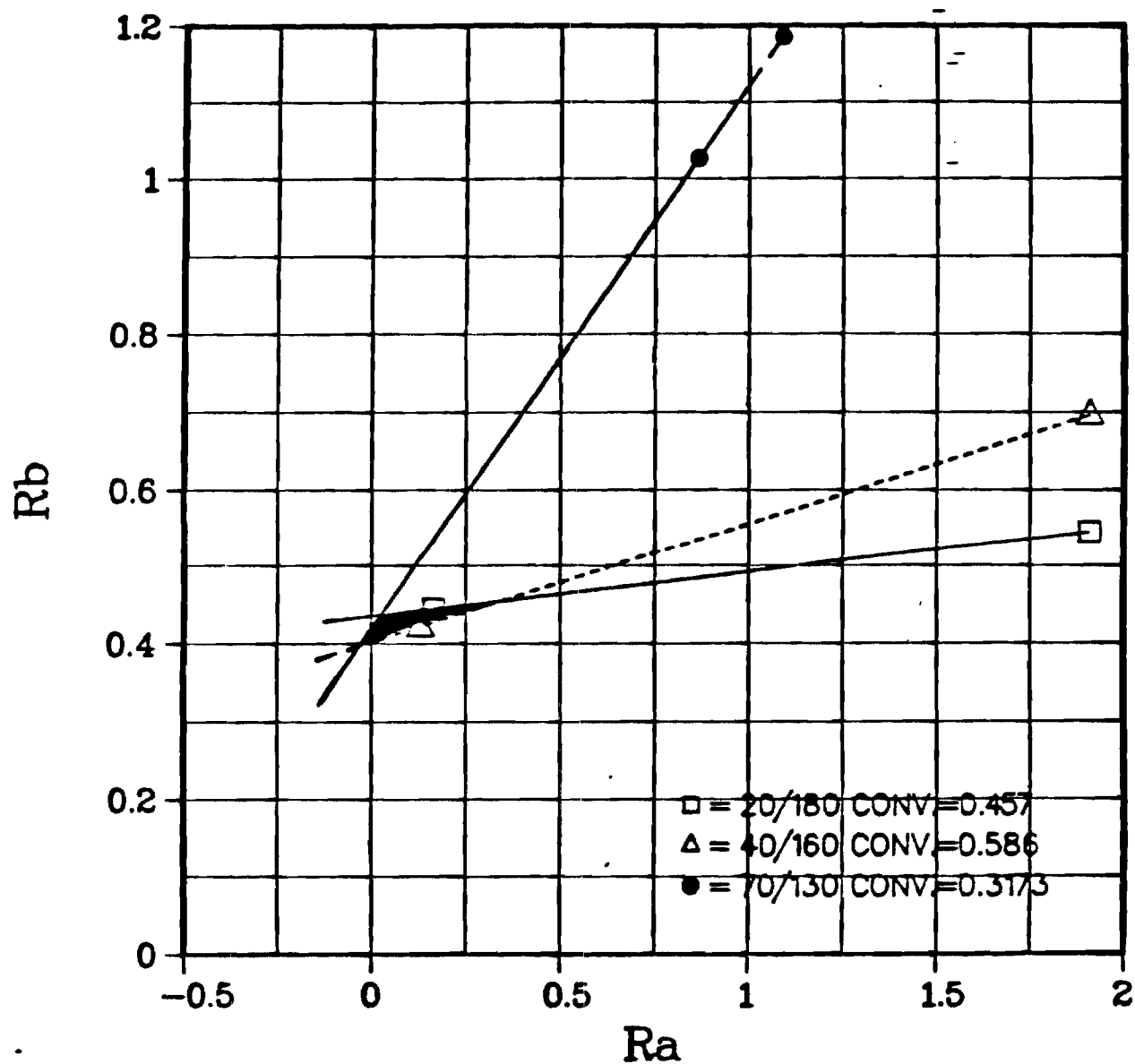


Figure 27: Reactivity ratios of MAA (R_a) and styrene (R_b) based on the Mayo-Lewis approach.

REACTION RATES OF CLEANED AND UNCLEANNED MONOMERS

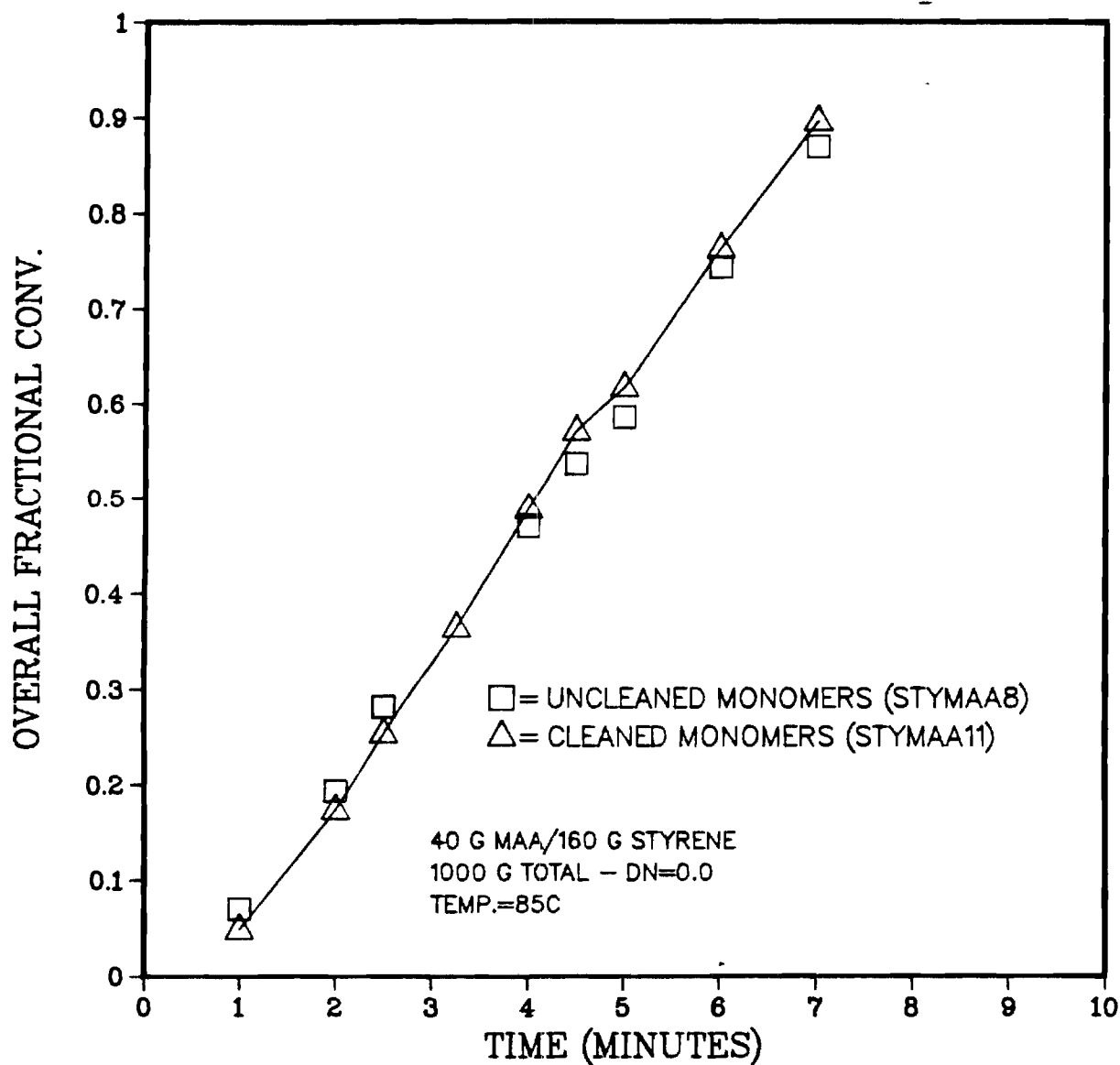


Figure 28: Comparison of reaction rates with cleaned and uncleaned monomers. MAA/styrene system with a weight ratio of 40/160.

Initial Particle Size Measurements

Some particle size analysis has been performed using a Malvern light scattering device. The results are listed in Table 1. The large particle sizes and large standard deviations of the lower conversion samples suggest that particle stability is low at low conversion resulting in a significant amount of coagulation. Further discussion concerning the size of the particles will be made after results from HDC analysis become available for comparison to those obtained via the light scattering method.

Degree of Neutralization Overall and in the Aqueous Phase

The degree of neutralization (DN) of the acid monomer affects the partition of that monomer between the aqueous and organic phases. Figure 29 presented in the previous progress report reveals that the amount of acid monomer present in the organic phase decreases as the DN increases. The effect is greater for MAA than for AA. Another important point to consider is whether the acid that is present in the organic phase is neutralized to the same extent as that remaining in the aqueous phase.

The DN value presented in Figure 29 was based on the overall amount of acid used in the partition experiment. If the acid that partitions into the organic phase consists of the same fraction of neutralized species and thus the same DN as that based on the overall fraction of neutralized acid, then the acid remaining in the aqueous phase will, likewise, exhibit the same DN. Titration data discussed in the previous report was reexamined to determine whether the DN of acid in the aqueous phase was indeed the same as the DN overall (and thus the DN of acid in the organic phase).

Table 1: Particle size measurements of latexes obtained from emulsion copolymerization of AA/styrene and MAA/styrene in a seeded batch reaction.

System	Wt. Ratio	Sample	Conv.	Size (nm)	Std. Dev.
STY/AA-8	20/180	FP	0.97	93	26.8
STY/AA-5	40/160	3	0.31	63	48.9
		9	0.86	70	35.1
		FP	0.97	80	22.6
STY/AA-6	70/130	2	0.13	82	65
		6	0.50	67	36
		10	0.86	83	25.1
		FP	0.98	123	49.1
STM10-SD		SEED		48	38.1
STY/MAA-10	20/180	3	0.1057	1750	2080
		6	0.42	63	32.9
		9	0.60	64	23.9
		FP	0.96	74	27.9
STY/MAA-8	40/160	FP	0.95	100	28.3
STY/MAA-9	70/130	2	0.12	140	112.1
		5	0.43	124	36.5
		9	0.79	78	35.5
		FP	0.99	98	42.2

MONOMER PARTITION AS A FUNCTION OF DN

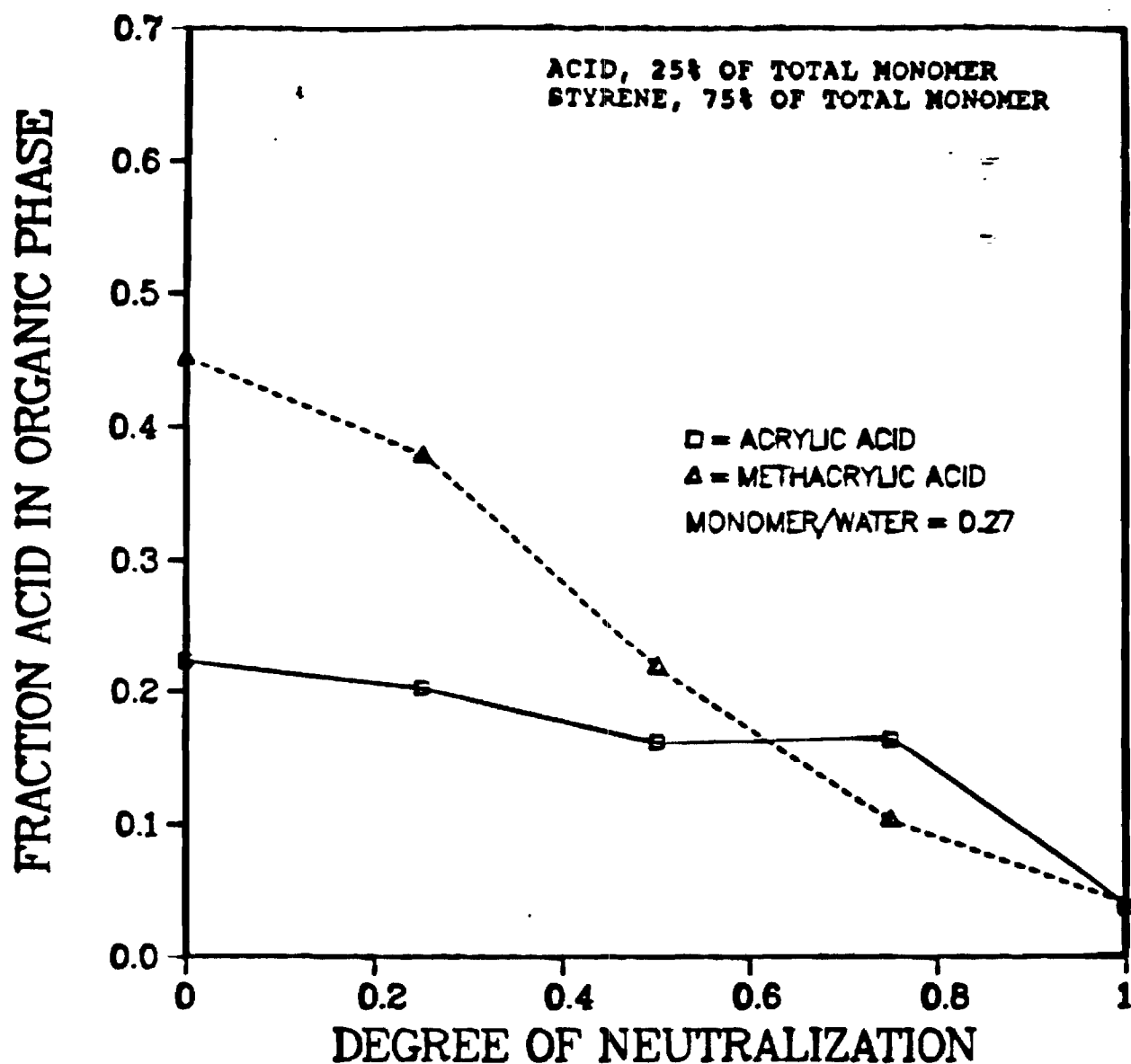


Figure 29: Partition of MAA and AA between the aqueous and organic phases at various degrees of neutralization.

An excess of strong acid (HCl) was added to each aqueous-phase sample. The samples were then titrated with a sodium hydroxide solution ($\sim 1.0M$) to detect two endpoints, one for the excess HCl, and one for the carboxylic acid monomer. The DN of the aqueous phase was then calculated in the following way.

$$Neutralized\ Acid_{aq.\ phase} = HCl\ added - NaOH\ Titrated_{Endpt.I} = A \quad (2)$$

$$Total\ Acid_{aq.\ phase} = NaOH\ Titrated_{Endpt.II-Endpt.I} = B \quad (3)$$

$$DN_{aq.\ phase} = A/B \quad (4)$$

The results of these calculations are shown in Figures 30 and 31 for MAA/styrene and AA/styrene, respectively.

The DN of the aqueous phase for the MAA/styrene system is higher than the overall DN. This fact suggests that the fraction of unneutralized acid species diffusing into the organic phase is greater than the fraction of unneutralized species present in the aqueous phase. The DN_{aq} for the AA/styrene system does not appear to be significantly different from the overall DN. However, since a smaller amount of AA partitions into the organic phase than does MAA, a change in DN_{aq} would not be as great as that for the MAA/styrene system even if the DN of the acid in the organic phase was near zero. Further analysis will be needed in order to make more quantitative conclusions. This information is important if one wishes to model the kinetic behavior of such a system since the propagation constants of the neutralized

PARTITION OF NaOH IN NEUTRALIZED ACID/STYRENE SYSTEMS

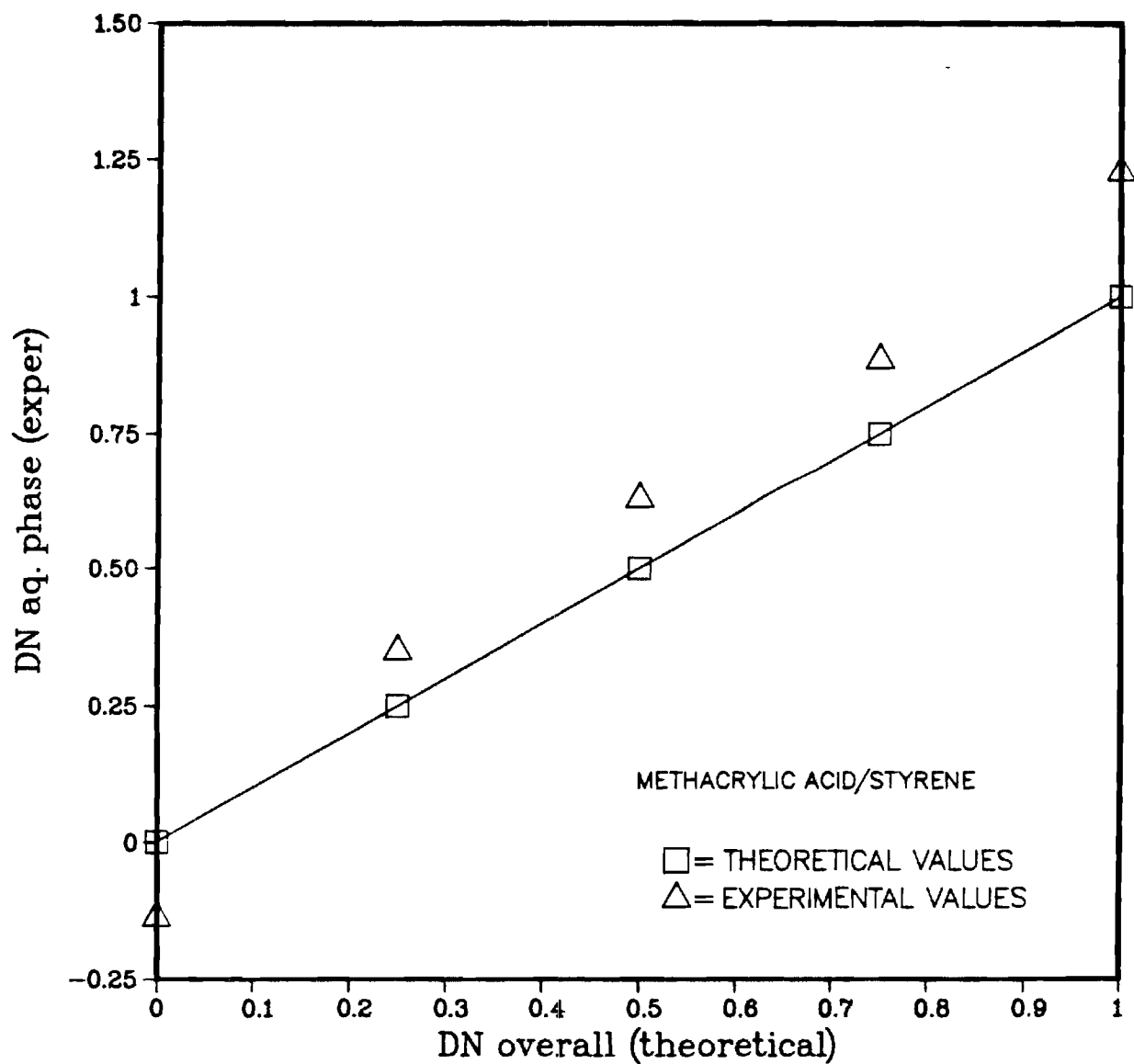


Figure 30: Comparison of DN in the aqueous phase to DN overall for the MAA/styrene system.

PARTITION OF NaOH IN NEUTRALIZED ACID/STYRENE SYSTEMS

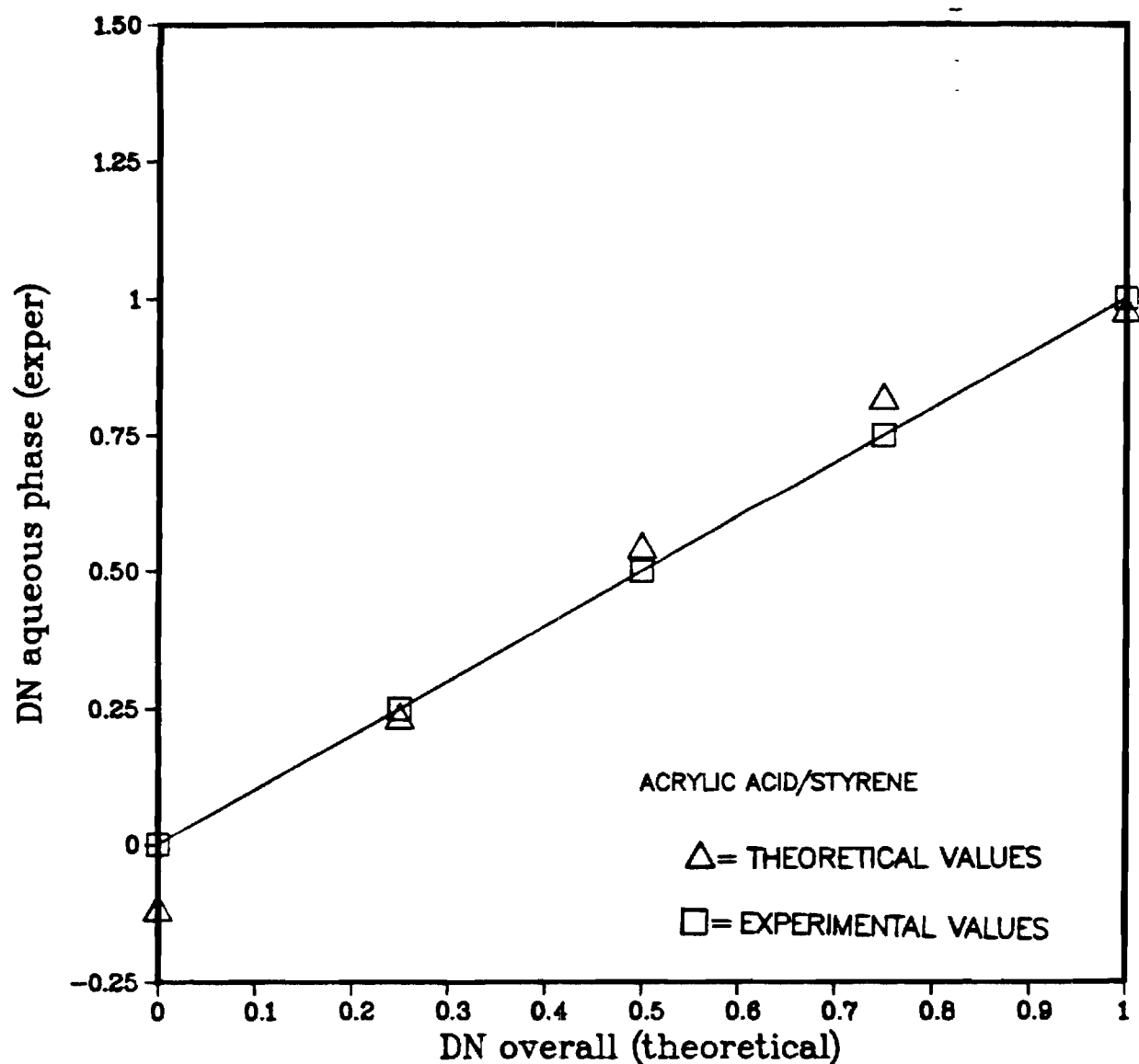


Figure 31: Comparison of DN in the aqueous phase to DN overall for the AA/styrene system.

and unneutralized acid species are different. (Experimental data addressing the reaction rates of the two species was presented in the previous report). Therefore, it is important to know the relative concentrations of each species in each phase.

Possible Approach to Modelling the Carboxylated Emulsion Copolymerization

Reaction at $DN > 0$

A possible kinetic model for the emulsion copolymerization of acid/styrene systems was outlined in the PhD proposal. An extension of this model to account for the dissociated acid species obtained when the acid has been partially neutralized is presented below.

Assume initially that the degree of neutralization of acid monomer is the same within the aqueous, droplet and particle phases. Define $DN = \text{moles NaOH}/\text{moles acid fed} = \alpha$. As long as the value of DN is greater than zero, then the system actually consists of three species: undissociated acid (A), styrene (B), and dissociated acid (C). The following equations may be used to express the reaction rates in the particles.

$$R_{pA} = k_{pAA}[M_A]_p \bar{n}_A \frac{N_T}{N_A} + k_{pBA}[M_A]_p \bar{n}_B \frac{N_T}{N_A} + k_{pCA}[M_A]_p \bar{n}_C \frac{N_T}{N_A} \quad (5)$$

$$R_{pB} = k_{pBB}[M_B]_p \bar{n}_B \frac{N_T}{N_A} + k_{pAB}[M_B]_p \bar{n}_A \frac{N_T}{N_A} + k_{pCB}[M_B]_p \bar{n}_C \frac{N_T}{N_A} \quad (6)$$

$$R_{pC} = k_{pCC}[M_C]_p \bar{n}_C \frac{N_T}{N_A} + k_{pAC}[M_C]_p \bar{n}_A \frac{N_T}{N_A} + k_{pBC}[M_C]_p \bar{n}_B \frac{N_T}{N_A} \quad (7)$$

where $[M_A]$ is the concentration of undissociated acid, $[M_B]$ is the concentration of styrene, $[M_C]$ is the concentration of dissociated acid, N_T is the number of

particles/ L_{aq} , k_{pij} is the propagation constant for radical i with monomer j , \bar{n}_j is the average number of j radicals/particle, and N_A is Avogadro's number.

The dissociated species, C, is treated like a third monomer in the above rate expressions. Nomura [2] gives expressions for the change in n_j with time for a copolymer system. Nomura's analysis may be extended to include the dissociated species, C. (See equation 8.)

$$\begin{aligned} \frac{d\bar{n}_A}{dt} = & \frac{\rho_e w_a}{N_T} - 2k_{tpAA} \frac{\bar{n}_A^2}{v_p} - k_{tpAB} \frac{\bar{n}_A \bar{n}_B}{v_p} - k_{tpAC} \frac{\bar{n}_A \bar{n}_C}{v_p} - k_{desA} \bar{n}_A \\ & - (k_{pAB} + k_{mAB}) [M_B]_p \bar{n}_A + (k_{pBA} + k_{mBA}) [M_A]_p \bar{n}_B \\ & - (k_{pAC} + k_{mAC}) [M_C]_p \bar{n}_A + (k_{pCA} + k_{mCA}) [M_A]_p \bar{n}_C = 0 \end{aligned} \quad (8)$$

where ρ_e is the rate of adsorption of radicals by the particles, w_A is the probability of adsorbed radicals becoming an A radical, k_{mij} and $k_{t,ij}$ are chain transfer and termination constants, respectively, and k_{des} is a desorption constant.

Similar equations may be written for $d\bar{n}_B/dt$ and $d\bar{n}_C/dt$. Summation of these equations gives equation 9.

$$\begin{aligned} \frac{d\bar{n}}{dt} = & \frac{d(n_A + n_B + n_C)}{dt} = \frac{\rho_e}{N_T} - 2k_{tpAA} \frac{\bar{n}_A^2}{v_p} - 2k_{tpAB} \frac{\bar{n}_A \bar{n}_B}{v_p} \\ & - 2k_{tpBB} \frac{\bar{n}_B^2}{v_p} - 2k_{tpAC} \frac{\bar{n}_A \bar{n}_C}{v_p} - 2k_{tpBC} \frac{\bar{n}_B \bar{n}_C}{v_p} - 2k_{tpCC} \frac{\bar{n}_C^2}{v_p} \\ & - (k_{desA} \bar{n}_A + k_{desB} \bar{n}_B + k_{desC} \bar{n}_C) \end{aligned} \quad (9)$$

Nomura notes that the termination and desorption terms in equation 9 are at most equal to ρ_e/N_T . If the rate of desorption is relatively small, $\rho_e \sim R_i$. w_A is less than unity. Therefore, Nomura states that the last terms (four in the above case) in equation 8 are dominating. ($\rho_e/N_T \approx 0.01$ to 1 and $k_p[M_i]_p \bar{n} \approx 100$ based on typical emulsion reaction systems.) The propagation constants are usually much greater in magnitude than the chain transfer rate constants ($k_p \gg k_m$) so 8 can be simplified to:

$$-k_{pAB}[M_B]_p \bar{n}_A + k_{pBA}[M_A]_p \bar{n}_B - k_{pAC}[M_C]_p \bar{n}_A + k_{pCA}[M_A]_p \bar{n}_C = 0 \quad (10)$$

Equilibrium between species A and C is described by equations 11 and 12.

$$[M_A] = (1 - \alpha)[M_A]_{tot} \quad (11)$$

$$[M_C] = \alpha[M_A]_{tot} \quad (12)$$

where α is the degree of neutralization or fraction of dissociation, and $[M_A]_{tot} = [M_A] + [M_C]$ is the total amount of acid species.

If this same relationship of dissociated and undissociated acid species applies to the radicals, (i.e. the presence or absence of a radical is assumed not to affect whether the carboxyl group is dissociated or undissociated) then,

$$\bar{n}_A = (1 - \alpha)\bar{n}_{A_{tot}} \quad (13)$$

$$\bar{n}_C = \alpha\bar{n}_{A_{tot}} \quad (14)$$

where $\bar{n}_{A_{tot}} = \bar{n}_A + \bar{n}_C$ is the total number of acid radicals.

Equation 10 may then be rewritten using the expressions given by equations 11 through 14. Rearrangement leads to the following expression.

$$A = \frac{\bar{n}_B}{\bar{n}_{A_{tot}}} = \frac{k_{p_{AB}}[M_B]_p + (k_{p_{CA}} - k_{p_{AC}})\alpha[M_A]_{tot}}{k_{p_{BA}}[M_A]_{tot}} \quad (15)$$

Then,

$$\bar{n}_{A_{tot}} = \frac{1}{1+A} \bar{n} \quad (16)$$

$$\bar{n}_A = (1-\alpha) \frac{1}{1+A} \bar{n} \quad (17)$$

$$\bar{n}_B = \frac{A}{1+A} \bar{n} \quad (18)$$

$$\bar{n}_C = \alpha \frac{1}{1+A} \bar{n} \quad (19)$$

Finally,

$$R_{p_A} = (k_{p_{AA}} \frac{1-\alpha}{1+A} + k_{p_{BA}} \frac{A}{1+A} + k_{p_{CA}} \frac{\alpha}{1+A}) (1-\alpha) [M_A]_{p_{tot}} \bar{n} \frac{N_T}{N_A} \quad (20)$$

$$R_{p_B} = (k_{p_{BB}} \frac{A}{1+A} + k_{p_{AB}} \frac{1-\alpha}{1+A} + k_{p_{CB}} \frac{\alpha}{1+A}) [M_B]_{p_{tot}} \bar{n} \frac{N_T}{N_A} \quad (21)$$

$$R_{p_C} = (k_{p_{CC}} \frac{\alpha}{1+A} + k_{p_{AC}} \frac{1-\alpha}{1+A} + k_{p_{BC}} \frac{A}{1+A}) \alpha [M_A]_{p_{tot}} \bar{n} \frac{N_T}{N_A} \quad (22)$$

Reactions run at $DN = 0$ and $DN = 1$ may be used to provide reactivity ratios and thus cross-propagation constants. Reaction rates may be obtained from two measurable parameters, $[M_A]_{p_{tot}}$ and $[M_B]_{p_{tot}}$. $[M_A]_{p_{tot}}$ may be determined by GC

analysis after separation of the aqueous and particle phases. Trifluoroacetic acid can be added to associate all of the acid monomer. (Acid monomer in the anionic form yields a salt with Na^+ which will not volatilize in the GC.) The concentration of the dissociated and associated monomers can then be calculated from $[\text{M}_A]_{\text{tot}}$ with equations 11 and 12. $[\text{M}_B]_{\text{overall}}$ may be measured directly with the GC. Partition information may then be used to determine $[\text{M}_B]_p$.

Reaction Rate in the Aqueous Phase with $\text{DN} > 0$

The reaction rate in the aqueous phase is given by equation 23.

$$\begin{aligned}
 R_{P_{aq}} &= -\left(\frac{d[A] + d[B] + d[C]}{dt}\right) = -\left(\frac{d[A]_{\text{tot}} + d[B]}{dt}\right) \\
 &= k_{AA}[A\cdot][A] + k_{AB}[A\cdot][B] + k_{AC}[A\cdot][C] \\
 &\quad + k_{BB}[B\cdot][B] + k_{BA}[B\cdot][A] + k_{BC}[B\cdot][C] \\
 &\quad + k_{CC}[C\cdot][C] + k_{CA}[C\cdot][A] + k_{CB}[C\cdot][B]
 \end{aligned} \tag{23}$$

A steady-state concentration is assumed for each type of radical.

$$k_{AB}[A\cdot][B] + k_{AC}[A\cdot][C] = k_{BA}[B\cdot][A] + k_{CA}[C\cdot][A] \tag{24}$$

$$k_{BA}[B\cdot][B] + k_{BC}[B\cdot][C] = k_{AB}[A\cdot][B] + k_{CB}[C\cdot][B] \tag{25}$$

$$k_{CA}[C\cdot][A] + k_{CB}[C\cdot][B] = k_{AC}[A\cdot][C] + k_{BC}[B\cdot][C] \tag{26}$$

In bulk or solution polymerizations the next step is to set the rate of initiation equal to the rate of termination.

$$R_i = R_{term}$$

However, in emulsion polymerization capture and desorption of radicals must be taken into account.

$$R_i = R_{term} + R_{capture} - R_{des}$$

Substitution of the appropriate expression leads to equation 27.

$$R_i = 2\bar{k}_{t_{ABC}}([A\cdot] + [B\cdot] + [C\cdot])^2 + \bar{k}_c([A\cdot] + [B\cdot] + [C\cdot])N_p - \frac{\bar{k}_{des}N_p\bar{n}}{N_A} \quad (27)$$

where $\bar{k}_{t_{ABC}}$ is an average termination constant dependent on DN, and \bar{k}_c is an average capture constant. Since $[A\cdot]_{tot} = [A\cdot] + [C\cdot]$, rearrangement gives equation 28.

$$\begin{aligned} [R_{tot}]_w &= ([A\cdot]_{tot} + [B\cdot]) \\ &= \frac{[-\bar{k}_cN_p + \sqrt{(\bar{k}_cN_p)^2 + 4(2\bar{k}_{t_{ABC}}(R_i + \bar{k}_{des}N_p\bar{n}/N_A))}]}{4\bar{k}_{t_{ABC}}} \end{aligned} \quad (28)$$

Expressions for $[A\cdot]$ and $[C\cdot]$ may now be obtained as follows.

$$[A\cdot] = (1 - \alpha)[A\cdot]_{tot} \quad (29)$$

$$[C\cdot] = \alpha[A\cdot]_{tot} \quad (30)$$

Substitution of equations 29 and 30 into equation 24 then rearrangement leads to expressions for $[A\cdot]_{tot}$ and $[B\cdot]$.

$$[A\cdot]_{tot} = \frac{[R_{tot}]_w}{1 + G} \quad (31)$$

$$[B\cdot] = \frac{[R_{tot}]_w G}{1 + G} \quad (32)$$

where

$$G = \frac{(1 - \alpha)(k_{AB}[B] + k_{AC}\alpha[A]_{tot}) - k_{CA}\alpha^2[A]_{tot}}{k_{BA}\alpha[A]_{tot}} \quad (33)$$

Substitution of these expressions for the total acid and styrene radicals into the following equation 34, gives a final expression for the rate of reaction in the aqueous phase which involves only two measurable parameters ($[M_A]_{tot}$ and $[M_B]$), but which accounts for the reaction of three different species (providing that the DN in each phase is known).

$$\begin{aligned} R_{p_{aq}} = & [k_{AA}(1 - \alpha)^2 + (\frac{k_{AA}}{r_{AC}} + \frac{k_{CC}}{r_{CA}})\alpha(1 - \alpha) + k_{CC}\alpha^2][A\cdot]_{tot}[A]_{tot} \\ & + [\frac{k_{AA}}{r_{AB}}(1 - \alpha) + \frac{k_{CC}}{r_{CB}}\alpha][A\cdot]_{tot}[B] \\ & + [\frac{k_{BB}}{r_{BA}}(1 - \alpha) + \frac{k_{BB}}{r_{BC}}\alpha][B\cdot][A]_{tot} + k_{BB}[B\cdot][B] \end{aligned} \quad (34)$$

Initial partition experiments suggest that the DN (or α) in the aqueous and organic phases may not be the same (especially with the MAA/styrene system). If the DN values are shown to be different in the two phases, the above equations will still apply as long as the proper values of α for each phase are used.

Future Work

The next phase of this research will be focused on obtaining more detailed partition information. Separation of the aqueous phase from the particle and droplet phase will be attempted using Nuclepore polycarbonate filters placed in stirred filter cells. Separation of the particle phase from the droplet and aqueous phases will be attempted using Nuclepore polyester filters also in stirred filter cells. The polycarbonate filters are hydrophilic and styrene does not easily penetrate the membrane. The polyester filters will probably allow both the aqueous phase and styrene droplets to pass through the membrane. Hopefully, these experiments will provide some of the information needed to better understand where the monomers are located during the reaction period.

Additional reactions involving the AA/styrene and MAA/styrene systems will be performed. Some reactions utilizing quantities of acid more typical to those found in 'industrial' recipes (i.e. 1 to 4% based on total monomer) may be investigated. Experiments which will help provide estimates for capture and desorption constants in these systems also need to be developed. Some continuous reactions could be helpful in this area. Mathematical modelling of the kinetic behavior of these reaction systems will also continue to be pursued.

References

1. H. Schuller, Polymer Reaction Engineering, Huthig and Wepf., Germany (1986).
H. Reichert and W. Geiseler, eds.
2. M. Nomura, M. Kubo, K. Fujita, J. Appl. Polym. Sci., 28, 2767 (1983).
3. L. Jansson, Masters Thesis, ChE Dept., Georgia Institute of Technology, (1983).